

Supporting Information

Synthesis of 2-Hydroxymethyl Ketones by Ruthenium Hydride-Catalyzed Cross-Coupling Reaction of α,β -Unsaturated Aldehydes with Primary Alcohols

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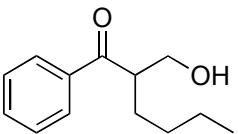
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General information. ^1H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer in CDCl_3 and are referenced at 0.00 ppm for TMS. Chemical shifts are reported in parts per million (δ). ^{13}C NMR spectra were recorded with a JEOL JMN-500 (125 MHz) spectrometer in CDCl_3 and are referenced at 77 ppm for CDCl_3 . Infrared spectra were obtained on a JASCO FT/IR-4100 spectrometer; absorptions were reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ was purchased from Wako Pure Chemical Industries, Ltd. Enals were distilled prior to use. The products were purified by flash chromatography on silica gel (Nacalai Tesque Inc., Silica Gel 60, 230-400 mesh) and/or preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) with GPC columns using CHCl_3 as an eluent.

Typical procedure for the cross-coupling reaction:

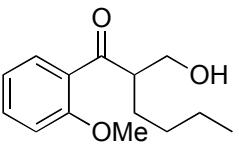
A mixture of benzyl alcohol (**1a**, 103.6 mg, 0.96 mmol), benzaldehyde (9 mg, 0.085 mmol) and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (77.2 mg, 0.081 mmol) in benzene (4 mL) are heated at reflux under nitrogen. A solution of 2-hexenal (**2a**, 78.1 mg, 0.80 mmol) in benzene (5 mL) was added during 1 h by a syringe pump. Then the resulting mixture was stirred another 1 h under reflux. Purification by recycling HPLC gave the product **3a** (119 mg, 72%) as a colorless oil.

2-Hydroxymethyl-1-phenyl-1-hexanone (**3a**):

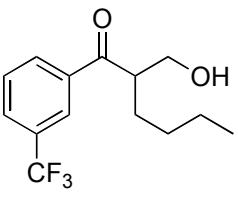

 ^1H NMR (500 MHz, CDCl_3) δ 0.86 (t, $J = 6.9$ Hz, 3H), 1.23-1.37 (m, 4H), 1.58-1.76 (m, 2H), 2.36 (br, 1H), 3.58-3.63 (m, 1H), 3.83-3.86 (m, 1H), 3.92-3.97 (m, 1H), 7.47-7.50 (m, 2H), 7.57-7.60 (m, 1H), 7.96-7.97 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.85, 22.78, 28.94, 29.56, 48.13, 62.97, 128.34, 128.74, 133.26, 136.81, 204.70; IR (neat): 3429, 1672 cm^{-1} ; EIMS m/z (relative intensity) 206 (M^+ , 8), 188 (15), 150 (71), 123 (56), 105 (100), 77 (63); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.1307, found: 206.1314.

Cignarella, G.; Barlocco, D.; Curzu, M.M.; Pinna, G.A. *Synthesis* **1984**, 342-5

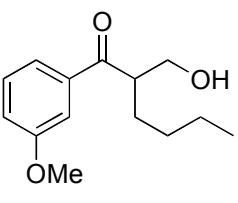
2-Hydroxymethyl-1-(2-methoxyphenyl)-1-hexanone (3b):

 ¹H NMR (500 MHz, CDCl₃) δ 0.85 (t, *J* = 6.9 Hz, 3H), 1.22-1.40 (m, 4H), 1.50-1.58 (m, 1H), 1.63-1.72 (m, 1H), 2.38 (t, *J* = 6.0 Hz, 1H), 3.57-3.63 (m, 1H), 3.83-3.88 (m, 2H), 3.88 (s, 3H), 6.96 (d, *J* = 8.7 Hz, 1H), 7.02 (t, *J* = 8.7 Hz, 1H), 7.45-7.49 (m, 1H), 7.60 (dd, *J* = 7.8, 1.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.81, 22.66, 28.06, 29.51, 52.68, 55.43, 62.50, 111.47, 120.77, 128.43, 130.21, 133.33, 157.93, 207.24; IR (neat): 3433, 1669 cm⁻¹; EIMS *m/z* (relative intensity) 236 (M⁺, 3), 187 (12), 135 (100); HRMS (EI) *m/z* calcd for C₁₄H₂₀O₃: 236.1412, found: 236.1412.

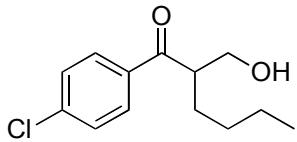
2-Hydroxymethyl-1-(3-trifluoromethylphenyl)-1-hexanone (3c):

 ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.25-1.38 (m, 4H), 1.57-1.75 (m, 2H), 2.09 (t, *J* = 6.4 Hz, 1H), 3.59-3.64 (m, 1H), 3.84-3.90 (m, 1H), 3.95-4.02 (m, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H) 8.22 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 13.65, 22.64, 28.81, 29.38, 48.59, 63.05, 123.60 (q, *J* = 270.8 Hz), 125.07, 129.32, 129.48, 131.10, 131.43, 137.58, 203.19. IR (neat): 3418, 1684 cm⁻¹; EIMS *m/z* (relative intensity) 274 (M⁺, 1), 256 (12), 218 (72), 173 (100), 145 (66); HRMS (CI) *m/z* calcd for C₁₄H₁₈F₃O₂(M⁺+H): 275.1259, found: 275.1261.

2-Hydroxymethyl-1-(3-methoxyphenyl)-1-hexanone (3d):

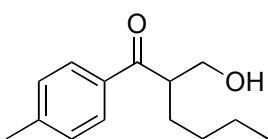
 ¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.27-1.38 (m, 4H), 1.60-1.76 (m, 2H), 2.36 (t, *J* = 6.0 Hz, 1H), 3.55-3.60 (m, 1H), 3.83-3.87 (m, 1H), 3.87 (s, 3H), 3.92-3.98 (m, 1H), 7.12-7.15 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.49 (s, 1H), 7.53-7.55 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.77, 22.70, 28.94, 29.46, 48.33, 55.32, 63.02, 112.58, 119.64, 120.90, 129.56, 138.23, 159.80, 204.36; IR (neat): 3434, 1676 cm⁻¹; EIMS *m/z* (relative intensity) 236 (M⁺, 15), 180 (21), 152 (36), 135 (100) 107 (20); HRMS (EI) *m/z* calcd for C₁₄H₂₀O₃: 236.1412, found: 236.1412.

1-(4-Chlorophenyl)-2-hydroxymethyl-1-hexanone (3e):



¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.24-1.40 (m, 4H), 1.57-1.73 (m, 2H), 2.16 (t, *J* = 6.0 Hz, 1H), 3.52-3.57 (m, 1H), 3.80-3.86 (m, 1H), 3.92-3.97 (m, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.71, 22.67, 28.89, 29.39, 48.34, 63.06, 128.88, 129.66, 135.29, 139.56, 203.28; IR (neat): 3425, 1675 cm⁻¹; EIMS *m/z* (relative intensity) 240 (M⁺, 1), 184 (30), 139 (100), 111 (28); HRMS (EI) *m/z* calcd for C₁₃H₁₇ClO₂: 240.0917, found: 240.0905.

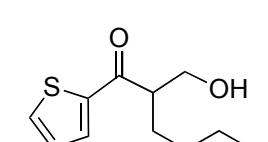
2-Hydroxymethyl-1-(4-methylphenyl)-1-hexanone (3f):



¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.25-1.39 (m, 4H), 1.57-1.75 (m, 2H), 2.31 (t, *J* = 6.0 Hz, 1H), 2.42 (s, 3H), 3.55-3.60 (m, 1H), 3.82-3.88 (m, 1H), 3.90-3.98 (m, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.87 (*J* = 8.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.73, 21.54, 22.68, 29.43, 47.98, 63.03, 128.39, 129.27, 134.35, 143.96, 204.16; IR (neat): 3433, 1666 cm⁻¹; EIMS *m/z* (relative intensity) 220 (M⁺, 3), 202 (34), 187 (56), 164 (25), 119 (100), 91 (59); HRMS (EI) *m/z* calcd for C₁₄H₂₀O₂: 220.1463, found: 220.1470.

2-Hydroxymethyl-1-(2-thienyl)-1-hexanone (3g):

A mixture of 2-thiophenecarboxyaldehyde (9.9 mg, 0.088 mmol) and RuHCl(CO)(PPh₃)₃ (76.1 mg, 0.08 mmol) in benzene (4 mL) was heated at reflux under nitrogen. A mixture of 2-hexenal (**2a**, 93 μL, 0.80 mmol) and 2-thiophenemethanol (**1g**, 91 μL, 0.96 mmol) in benzene (5 mL) was added during 1 h by a syringe pump. Then the resulting mixture was stirred another 30 min at reflux. Purification by recycling HPLC gave the product **3g** (110 mg, 64%) as a colorless oil.



¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.25-1.40 (m, 4H), 1.60-1.80 (m, 2H), 2.23 (t, *J* = 6.0 Hz, 1H), 3.38-3.43 (m, 1H), 3.80-3.88 (m, 1H), 3.89-3.95 (m, 1H), 7.15-7.17 (m, 1H), 7.68-7.69 (m, 1H), 7.76-7.77 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.78, 22.69,

29.21, 29.55, 50.22, 63.32, 128.27, 132.41, 134.32, 144.53, 197.05; IR (neat): 3433, 1647 cm⁻¹; EIMS *m/z* (relative intensity) 212 (M⁺, 6), 156 (44), 111 (100); HRMS (EI) *m/z* calcd for C₁₁H₁₆O₂S : 212.0871, found: 212.0867.

1-(2-Furanyl)-2-hydroxymethyl-1-hexanone (3h):

¹H NMR (500 MHz, CDCl₃) δ 0.88 (t, *J* = 7.4 Hz, 3H), 1.25-1.40 (m, 4H), 1.60-1.80 (m, 2H), 2.23 (t, *J* = 5.5 Hz, 1H), 3.35-3.40 (m, 1H), 3.78-3.84 (m, 1H), 3.88-3.94 (m, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 7.25 (d, *J* = 3.7 Hz, 1H), 7.62 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.72, 22.60, 28.61, 29.40, 49.21, 63.01, 112.30, 118.13, 146.85, 152.76, 192.84. IR (neat): 3434, 1660 cm⁻¹; EIMS *m/z* (relative intensity) 196 (M⁺, 2), 140 (100), 95 (96); HRMS (EI) *m/z* calcd for C₁₁H₁₆O₃: 196.1099, found: 196.1099.

2-Hydroxymethyl-1-phenyl-1-octanone (3i):

¹H NMR (500 MHz, CDCl₃) δ 0.85 (t, *J* = 7.4 Hz, 3H), 1.20-1.40 (m, 8H), 1.56-1.74 (m, 2H), 2.24-2.29 (m, 1H), 3.57-3.62 (m, 1H), 3.82-3.88 (m, 1H), 3.92-3.97 (m, 1H), 7.45-7.52 (m, 2H), 7.57-7.60 (m, 1H), 7.94-7.98 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.91, 22.45, 27.27, 29.19, 29.28, 31.47, 48.17, 62.98, 128.27, 128.63, 133.13, 136.86, 204.62; IR (neat): 3423, 1673 cm⁻¹; EIMS *m/z* (relative intensity) 234 (M⁺, 1), 150 (14), 120 (43), 105 (100), 77 (31); HRMS (EI) *m/z* calcd for C₁₅H₂₂O₂: 234.1620, found: 234.1616.

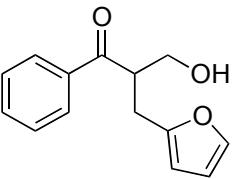
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¹H NMR (500 MHz, CDCl₃) δ 0.95 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 2.14 (t, *J* = 6.0 Hz, 1H), 2.22 (oct, *J* = 6.9 Hz, 1H), 3.43-3.49 (m, 1H), 3.80-3.86 (m, 1H), 4.03-4.10 (m, 1H), 7.47-7.50 (m, 2H), 7.57-7.60 (m, 1H), 7.95-7.97 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 19.69, 21.38, 28.55, 54.17, 61.27, 128.30, 128.63, 133.18, 137.77, 205.15; IR (neat): 3410, 1660 cm⁻¹; EIMS *m/z* (relative intensity) 192 (M⁺, 13),

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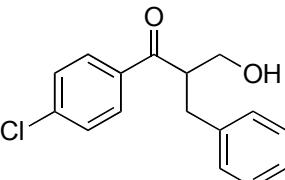
Kobayashi, S.; Hachiya, I. *J. Org. Chem.* **1994**, 59, 3590.

3-(2-Furanyl)-2-hydroxymethyl-1-phenyl-1-propanone (3k):

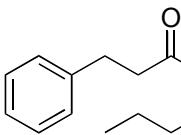
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1-(4-Chlorophenyl)-2-hydroxymethyl-3-phenyl-1-propanone (3l):

A mixture of 4-chlorobenzaldehyde (12 mg, 0.085 mmol) and RuHCl(CO)(PPh₃)₃ (73.5 mg, 0.077 mmol) in benzene (4 mL) was heated at reflux under nitrogen. A mixture of cinnamaldehyde (**2e**, 102 mg, 0.77 mmol) and 4-chlorobenzyl alcohol (**1e**, 132 mg, 0.93 mmol) in benzene (5 mL) was added during 1 h with a syringe pump. Then the resulting mixture was stirred another 1 h at reflux. Purification by recycling HPLC gave the product **3l** (147 mg, 69%) as a colorless oil.

 ¹H NMR (CDCl₃, 500 MHz) δ 2.17 (bs, 1H), 2.92 (dd, *J* = 13.8, 7.8 Hz, 1H), 3.21 (dd, *J* = 13.8, 6.4 Hz, 1H), 3.79-3.85 (m, 2H), 3.88-3.91 (m, 1H), 7.17-7.20 (m, 3H), 7.24-7.27 (m, 2H), 7.40-7.41 (m, 2H), 7.82-7.83 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 35.22, 50.29, 62.85, 126.76, 128.75, 129.07, 129.14, 129.94, 135.22, 138.72, 139.99, 202.81; IR (neat): 3433, 1676 cm⁻¹; EIMS *m/z* (relative intensity) 274 (M⁺, 8), 256 (17), 243 (66), 139 (100), 111 (36), 91 (32); HRMS (EI) *m/z* calcd for C₁₆H₁₅O₂Cl : 274.0761, found: 274.0763.

4-Hydroxymethyl-1-phenyl-3-octanone (3m):


¹H NMR (CDCl₃, 500 MHz) δ 0.86 (t, *J* = 6.9 Hz, 3H), 1.14-1.33 (m, 4H), 1.40-1.47 (m, 1H), 1.51-1.60 (m, 1H), 1.83 (bs, 1H), 2.64-2.69 (m, 1H), 2.80-2.84 (m, 2H), 2.90-2.93 (m, 2H), 3.68 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.76 (dd, *J* = 11.0, 7.8 Hz, 1H), 7.18-7.20 (m, 2H), 7.26-7.29 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 13.92, 22.87, 27.93, 29.59, 44.51, 54.03, 62.98, 126.25, 128.48, 128.61, 141.21, 214.06; IR (neat): 3437, 1707 cm⁻¹; EIMS *m/z* (relative intensity) 234 (M⁺, 17), 178 (32), 133 (28), 105 (75), 104 (61), 91 (100), 77 (14); HRMS (EI) *m/z* calcd for C₁₅H₂₂O₂: 234.1620, found: 234.1619.

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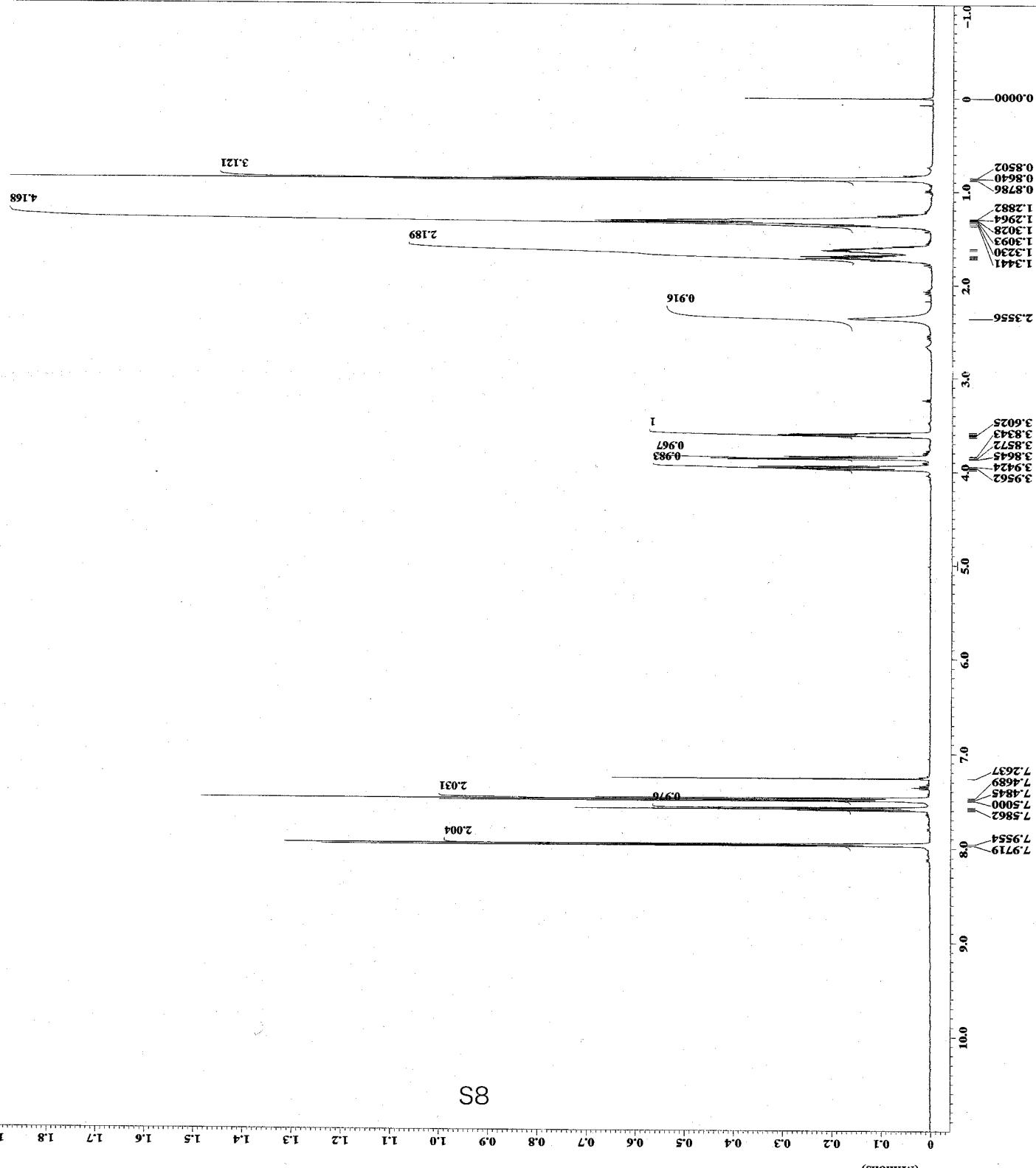
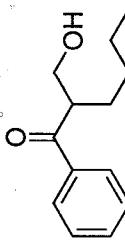
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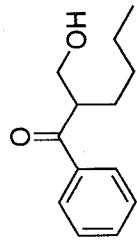
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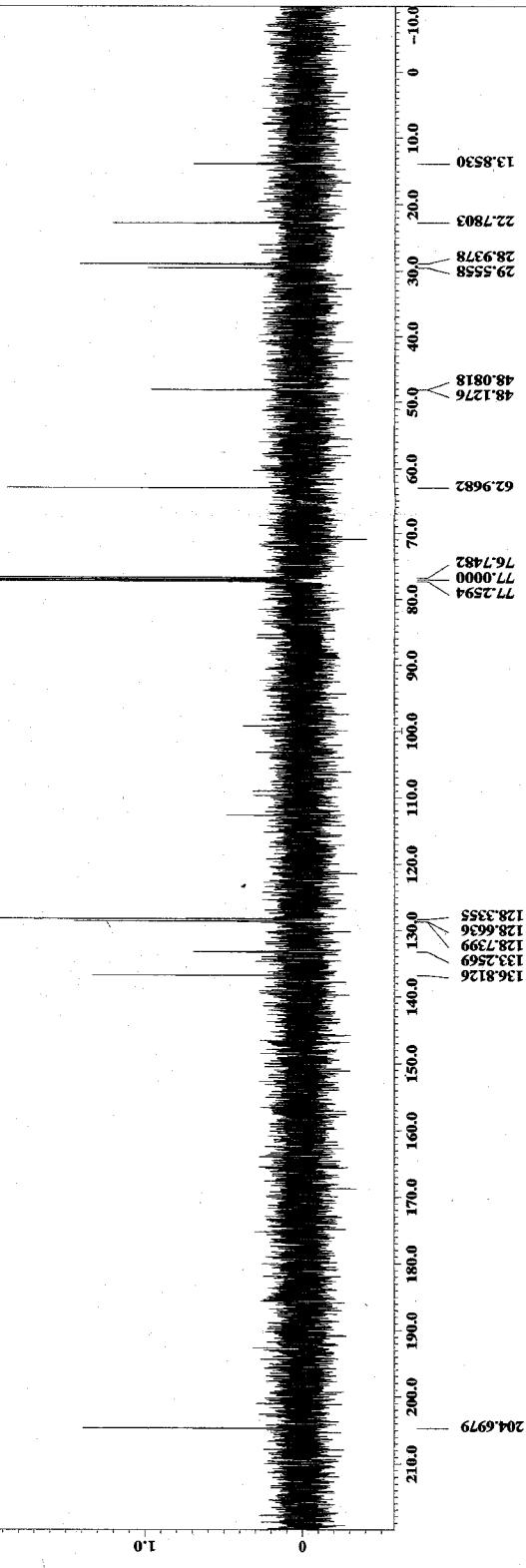


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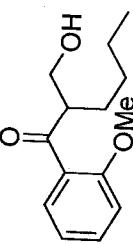


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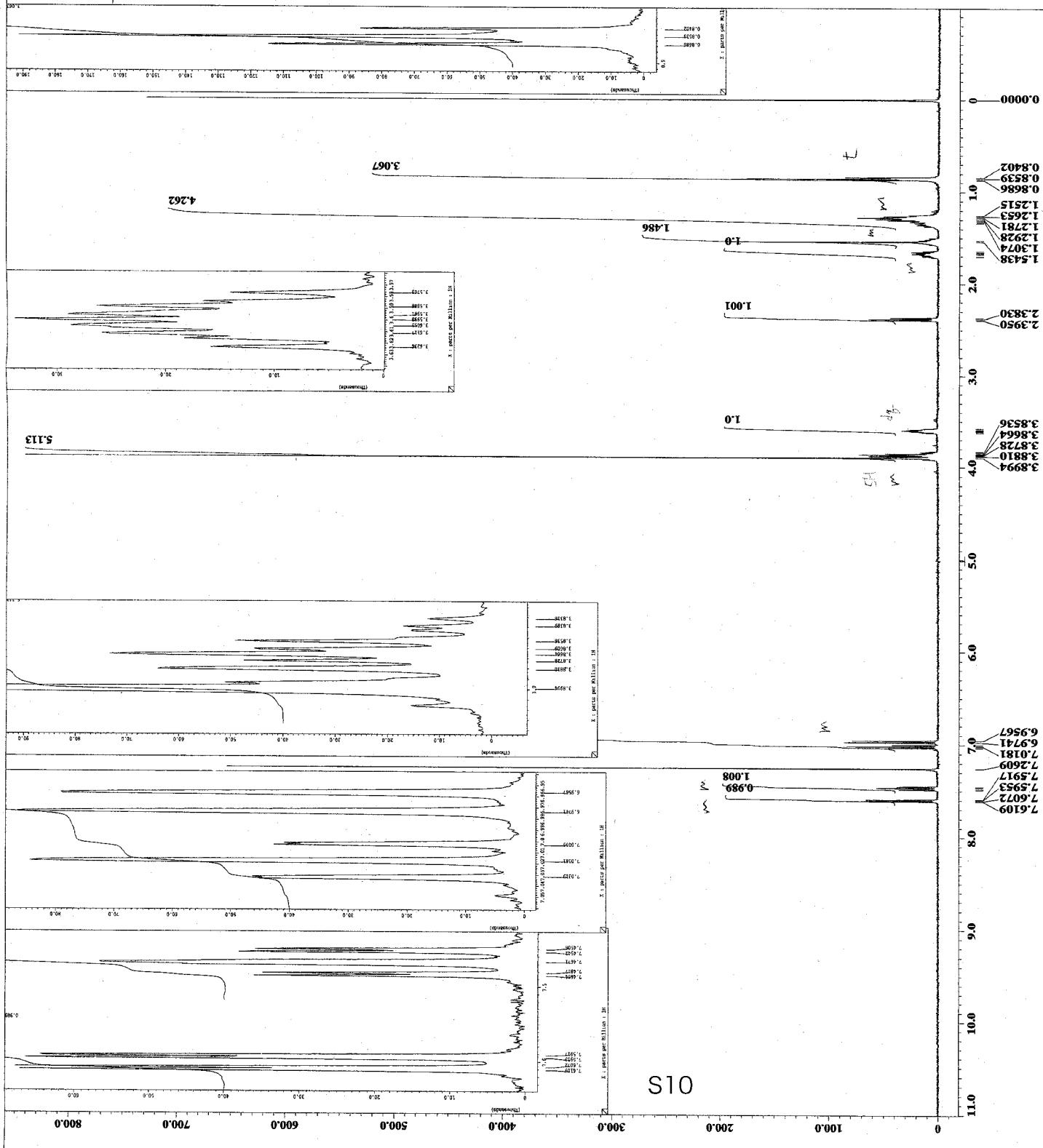


S9

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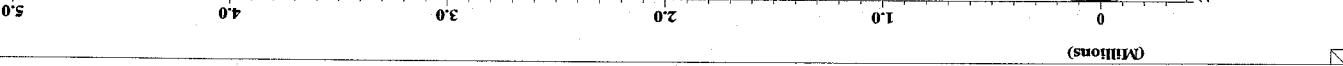
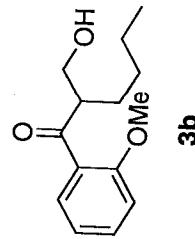
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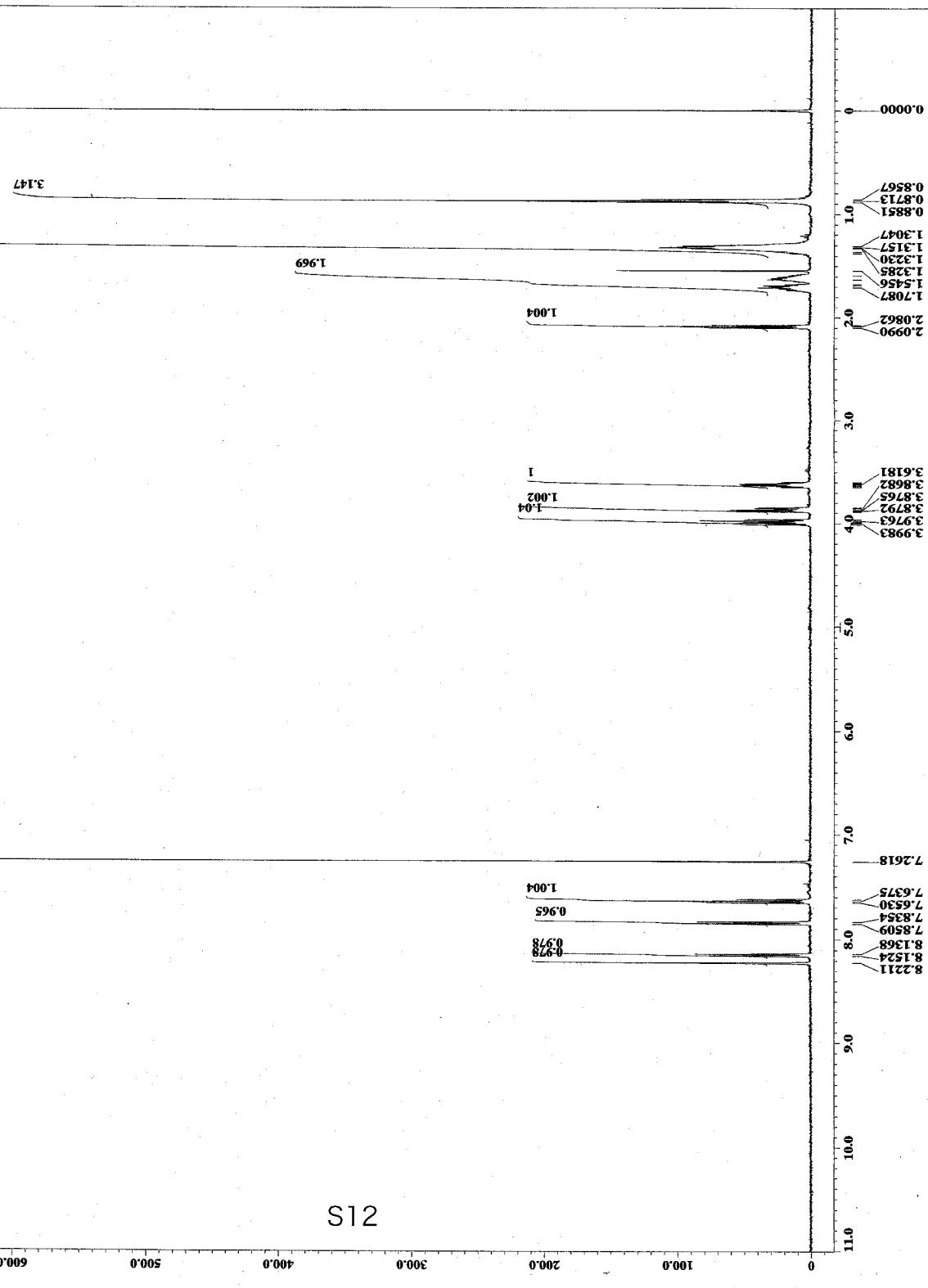
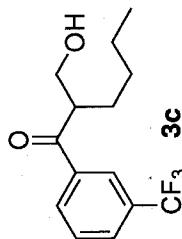
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----- SPECTRAL PARAMETERS -----
Spec Type = DELPA_NMR
Format = 1D COMPLEX
Dimensions = 1
Dim Title = 
Dim Size = 16384
Dim Units = [ppm]
Sampvol = 1.0
Pulse = 90.0
Acqtime = 0.0001
Recycle = 1.0
D1 = 0.01
D1Return = 0.0
D1Gated = 0.0
D1Wait = 0.0
K_offset = 0.0
K_free = 0.0
K_swexp = 0.0
Solvent = 
Spinbit = 1.0
Get = 24.0 [Hz]
Recur, Gain = 15.0
Pulsewidth = 10.0
Strength = 11.7473579 [T]
RFfilter, width = 3.75119336 [kHz]

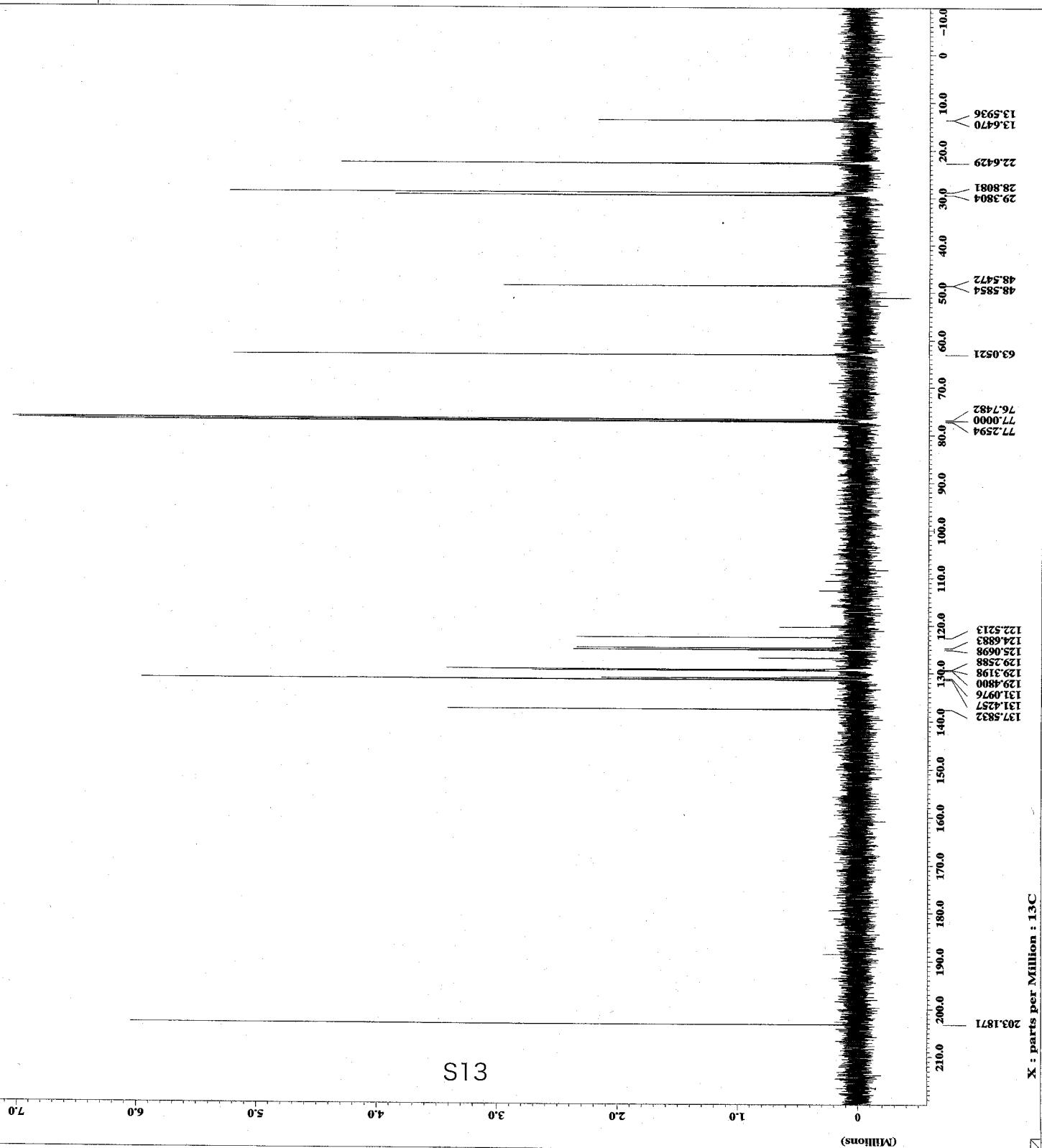
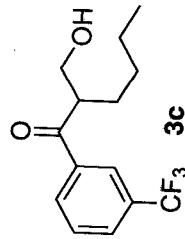
```



EJOL

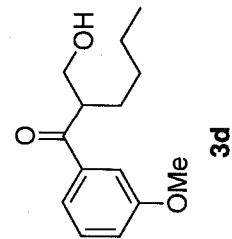
ACQUISITION PARAMETERS

File Name = 1d.13c.spectrum.84
 Author = 13C
 Sample ID = Single Pulse with Broad
 Content = 26-MAR-2007 15:30:27
 Creation Date = 30-MAR-2007 05:13:59
 Revision Date = ECP500
 Spec Site = DELTA NMR
 Spec Type = 1D COMPLEX
 Data Format = X
 Dimensions = 13C
 Dimittle = 32768
 Dim Units = [ppm]
 Scans = 200
 Mod return = 1.0c
 A_domain = 1.0c [ppm]
 T1spec = 125.778574 [Hz]
 T2spec = 31.44654088 [Hz]
 Solvent = CHLOROFORM-D
 Spin get = 17 [Hz]
 Temp_get = 25.2 [dc]
 Recvr_gain = 15
 Field_strength = 11.7473579 [mT]
 Filter_mode = BUTTERWORTH
 Filter_width = 15.7206621 [Hz]

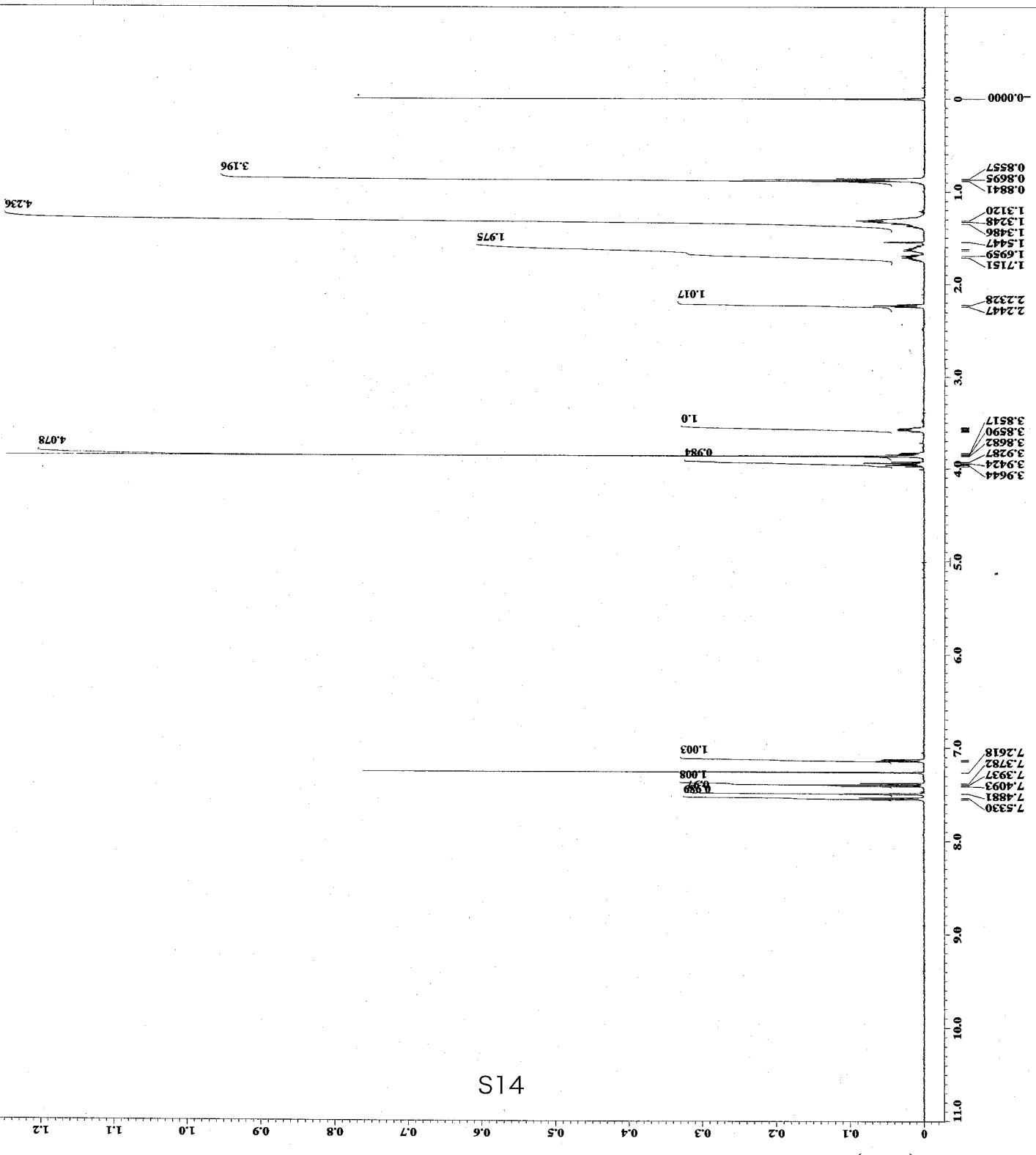


----- ACQUISITION PARAMETERS -----

File Name = 1d_spectra.m6
 Author ID = 1H
 Sequence ID = Single Pulse Experiment
 Comment =
 Creation Date = 16-MAR-2007 14:31:51
 Revision Date = 18-MAR-2007 03:59:00
 Spec Site = ECP500
 Spec Type = DELTA_NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 File Title = 1H
 File Size = 153.84
 File Units = [ppm]
 GcPointsTurn = 6
 NodTurn = 1
 ZGcTurn = 1H
 ZOffset = 51 [ppm]
 ZFreq = 500.162441602 [MHz]
 ZSweep = 7.50750751 [MHz]
 Solvent = CHLOROFORM-D
 SpinGet = 15 [Hz]
 TempGet = 24.3 [dc]
 Recv_Gain = 15
 Field_Strength = 11.7473579 [T]
 Filter_Mode = BUTTERWORTH
 Filter_Width = 3.75119936 [MHz]



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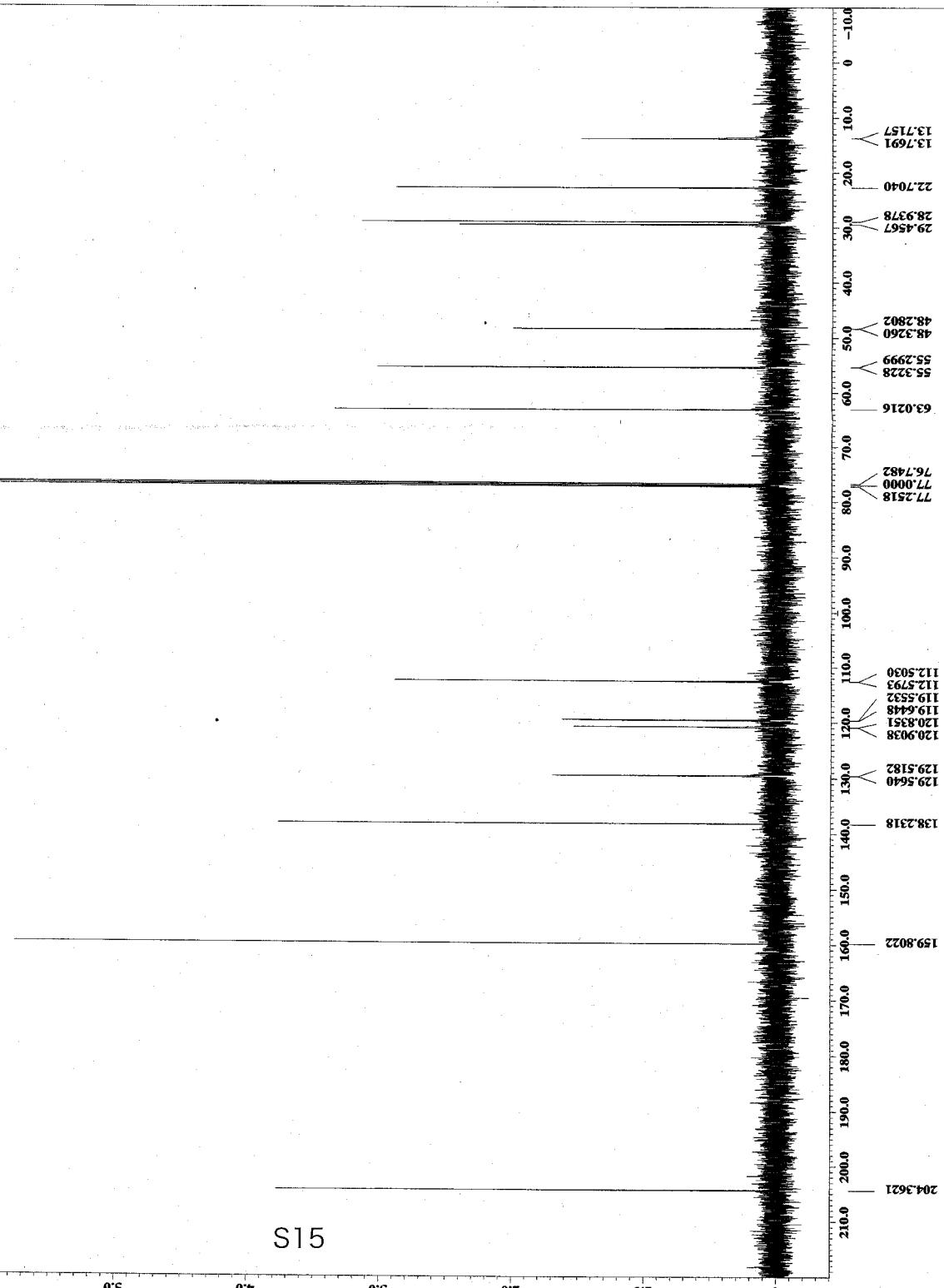
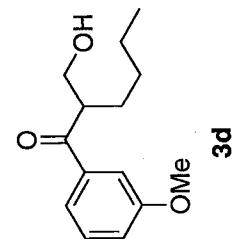


X : parts per Million : 1H

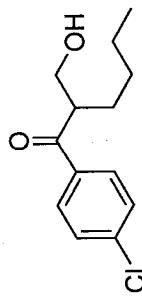
(Millions)

ACQUISITION PARAMETERS

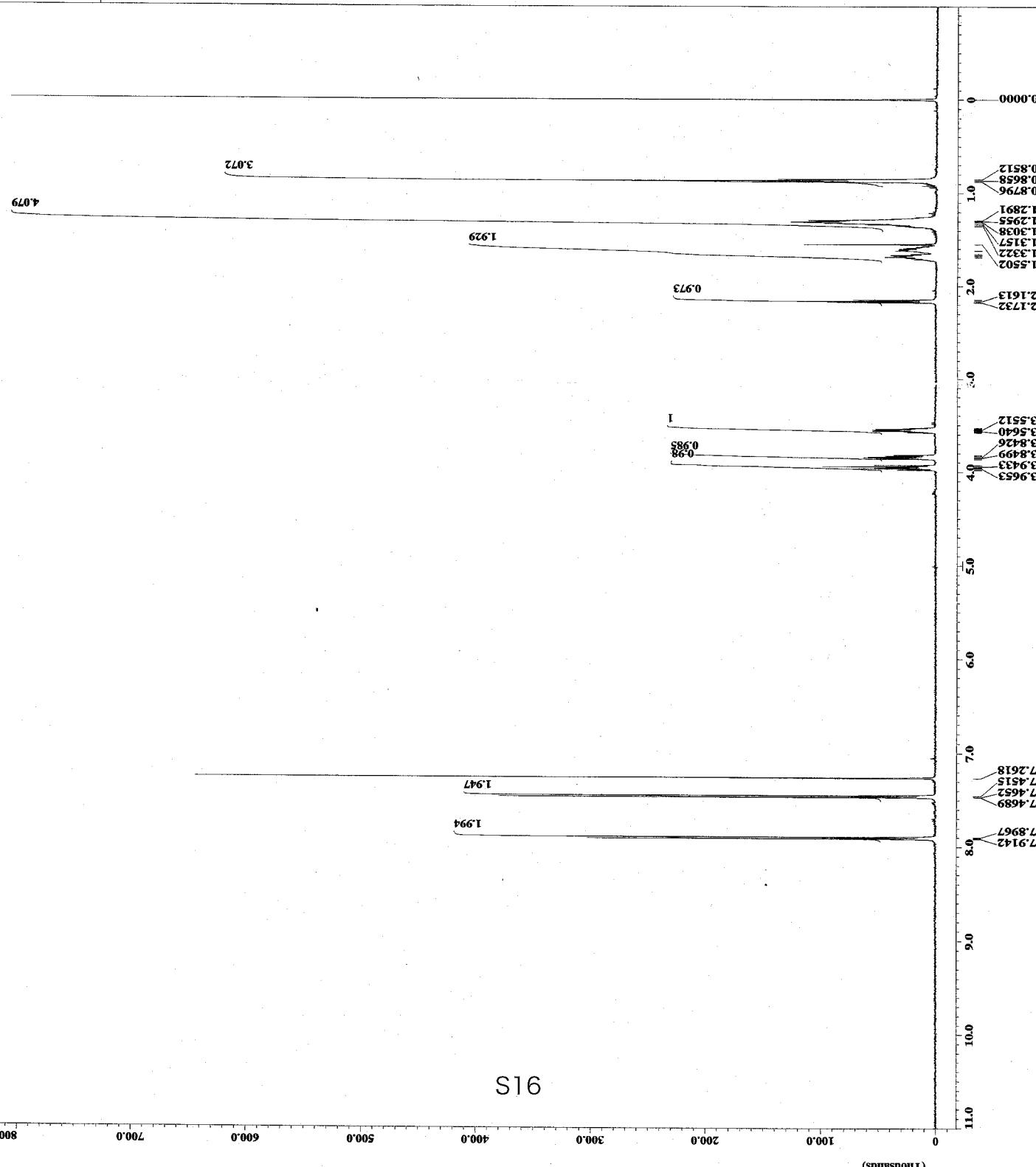
File Name = 1C_spectrum_81
 Author = 1C
 Sample ID = Single Pulse with Broad
 Created Date = 26-MAR-2007 15:15:42
 Revision Date = 30-MAR-2007 04:54:45
 Spec Site = ECPS50
 Spec Type = DELTA_NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim_Wtitle = 1C
 Dim_Size = 33768
 Dim_Units = [ppm]
 Scans = 100
 Mod_Return = 1C
 X_Offset = 100 [ppm]
 X_Traq = 125.77787547 [MHz]
 X_Sweep = 31.44654081 [GHz]
 Solvent = CHLOROFORM-D
 Spin_Set = 16 [Hz]
 Temp_Set = 25.2 [degC]
 Recv_Gain = 15
 Field_Strength = 11.7473579 [T]
 Filter_Mode = BUTTERWORTH
 Filter_Width = 15.7206221 [Hz]



----- ACQUISITION PARAMETERS -----
File Name = 1d_spectrum.36
Author =

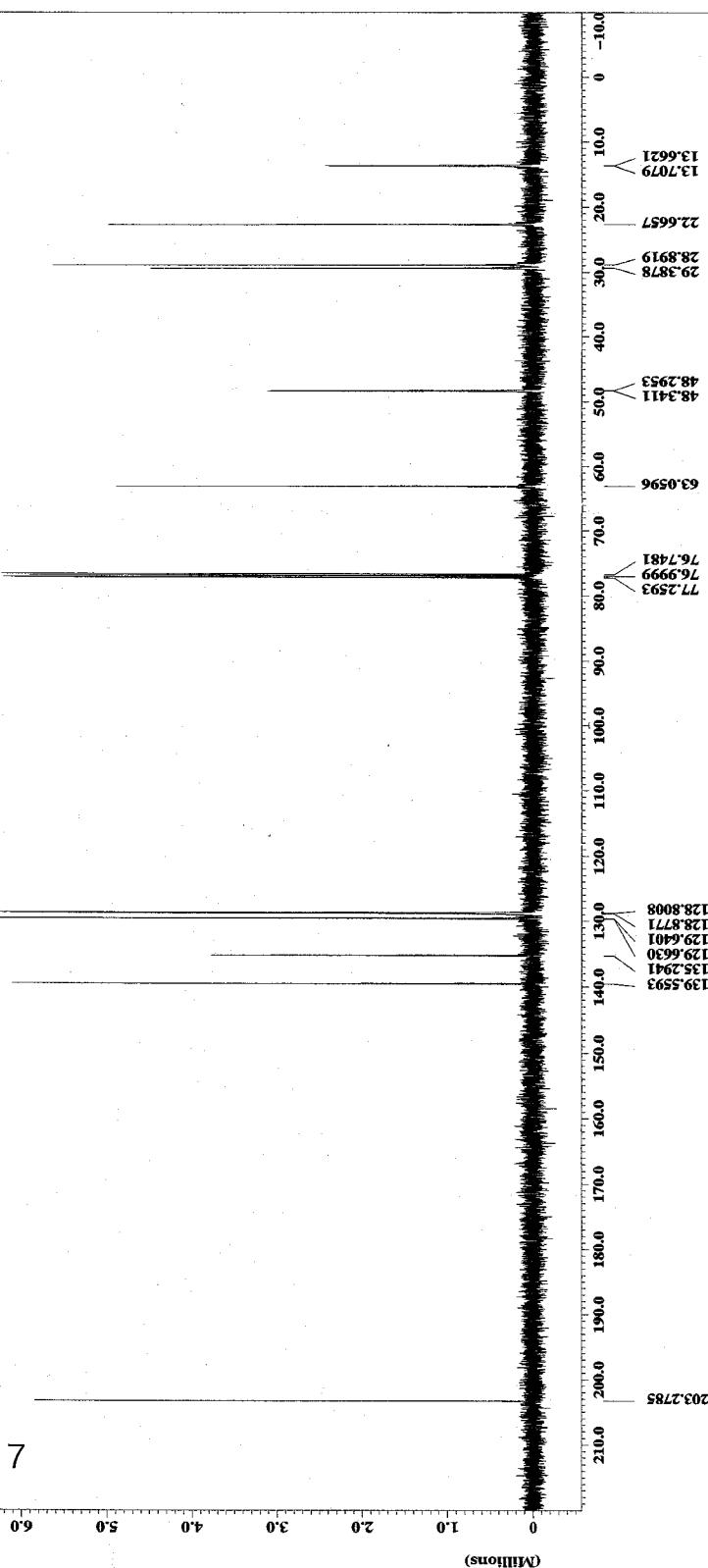
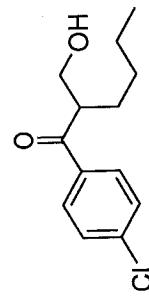


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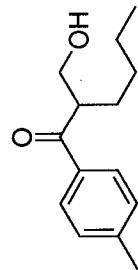
ACQUISITION PARAMETERS

P118 Name = 10_13C_specter.m75
 A sample ID = 13C
 Sample ID Content = Single Pulse, with Broad
 Creation Date = 26-MAR-2007 18:11:04
 Revision Date = 26-MAR-2007 07:55:36
 Spec Site = ECP500
 Spec Type = DATA_NMR
 Data Format = 1D_COMPLEX
 Dimensions = X
 Dim Title = 13C
 Dim Size = 3768
 Dim Units = [ppm]
 Scan_Units = 200
 Mod_Return = 1.
 X_domain = 13C
 X_Offset = 100 [ppm]
 X_Freq = 125.77787547 [MHz]
 X_Sweep = 31.4454081 [Hz]
 Solvent = CHLOROFORM-D
 Spin_get = 14 [Hz]
 Temp_get = 25.21 [dc]
 Recv_Gain = 15.
 Field_Strength = 11.7473579 [T]
 Filter_Modes = HOMOLUMINESCENCE
 Filter_Width = 15.7206622 [Hz]

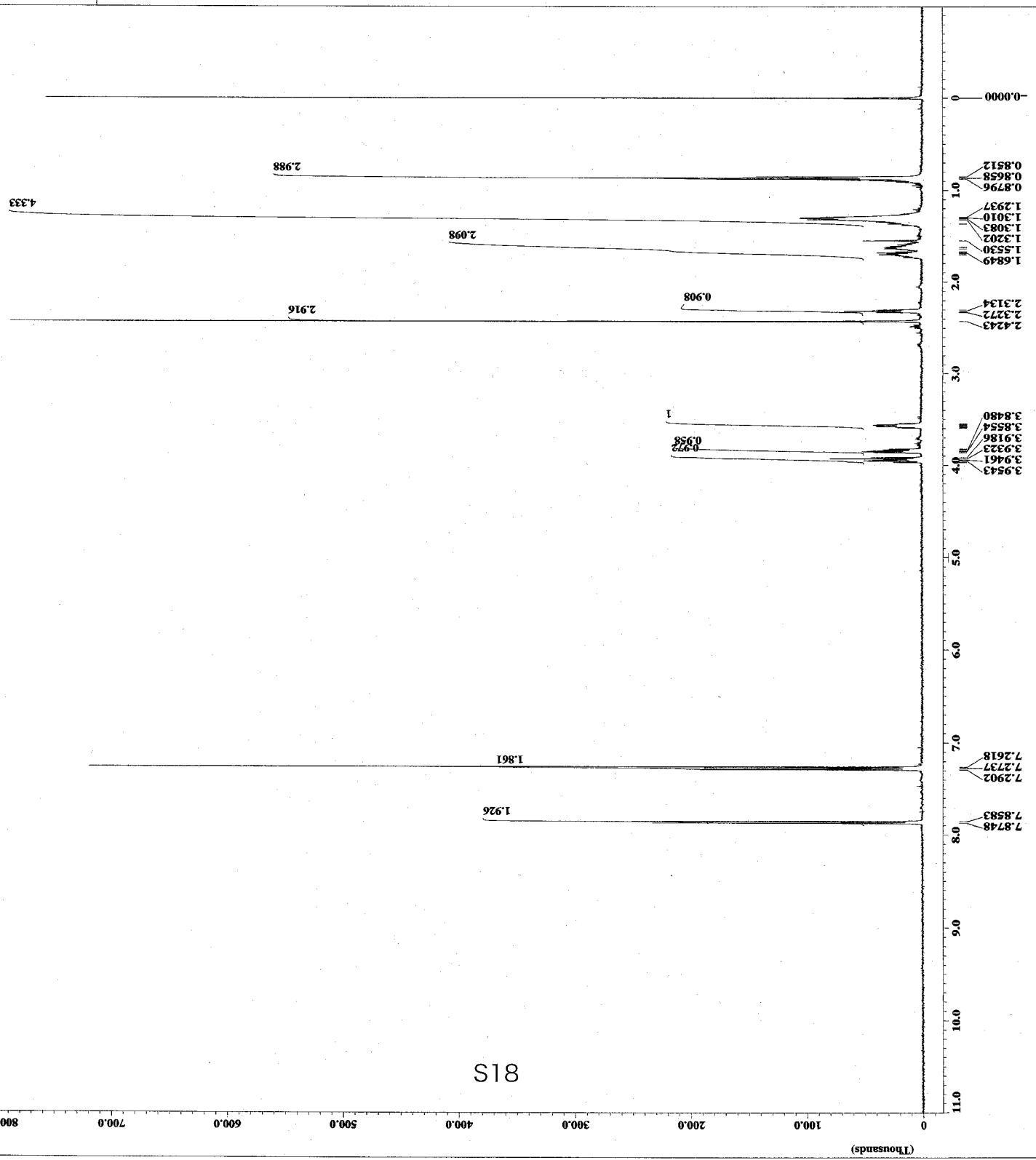


ACQUISITION PARAMETERS

File Name = 1H_Spectrum_4.19
 Sample ID = 1H
 Content = Single Pulse Experiment
 Creation Date = 16-MAR-2007 14:37:41
 Revision Date = 16-MAR-2007 04:06:36
 Spec Site = ECP500
 Spec Type = DEPTA_NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 1H
 Dim Size = 13384
 Dim Units = [ppm]
 ScanCount = 6
 No. of Return = 1
 X-domain = 1H
 X_Offset = 51[ppm]
 X_Freq = 501.16241602[NHz]
 X_Sweep = 7.50750751[KHz]
 Solvent = CHLOROFORM-D
 Spin_Set = 15 [Hz]
 Temo_Set = 24 [sec]
 Recv_Gain = 15
 Field_Strength = 11.7473579[G]
 Filter_Mode = SUPERWIDE
 Filter_Width = 3.75119936[Hz]



3f



ACQUISITION PARAMETERS -----
file Name = 1d_13c_spectrum.86

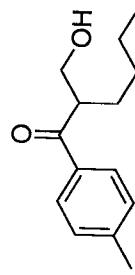
```

----- ACQUISITION PARAMETERS -----
File Name = 1d_13c_spectrum.s6
Author = 
Sample ID = 11C
Content Date = Single-Pulse 2007-03-20 15:47:27
Revision Date = 30-MAR-2007 05:34:36
Spec Site = EXP500

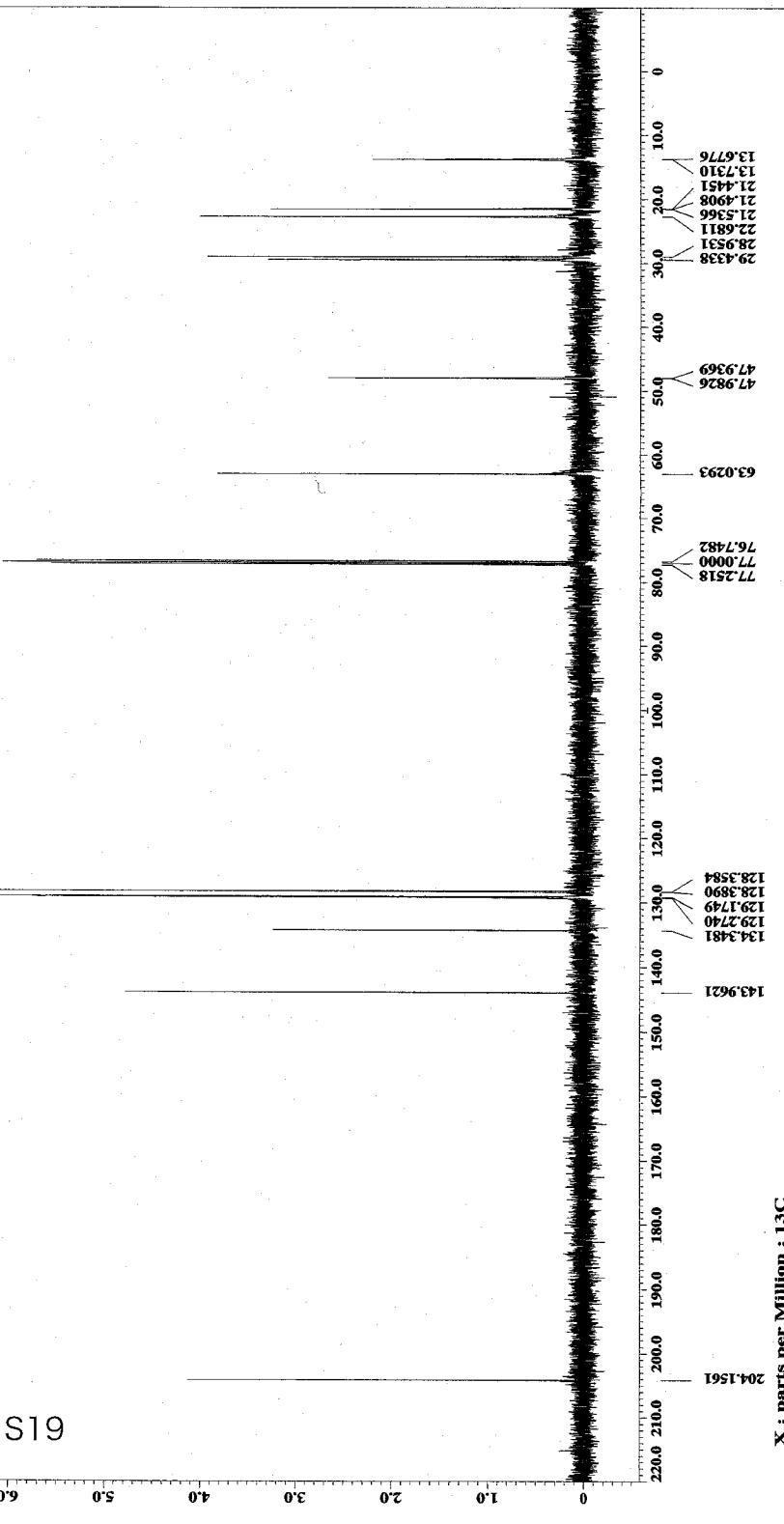
----- DATA -----  

Spec Type = DEPT_135R
Data Format = 1D COMPLEX
Dimensions = 1C
Dim Title = 
Dim Site = 177.68 [ppm]
Dim Units = [ppm]
Comments = 
Sweep Return = 1
X-domain = 1C
X_offset = 100 [ppm]
X_fref = 77.87547 [MHz]
X_sweep = 31.6464488 [MHz]
Solvent = CHLOROFORM-D
Spin.get = 24 [Hz]
Recv.get = 24.1 [mHz]
Recv.Gain = 15
Field.Strength = 11.7473579 [T]
Filter.mode = BUTTERWORTH
Filter.width = 15.7206621 [Hz]

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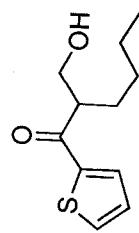


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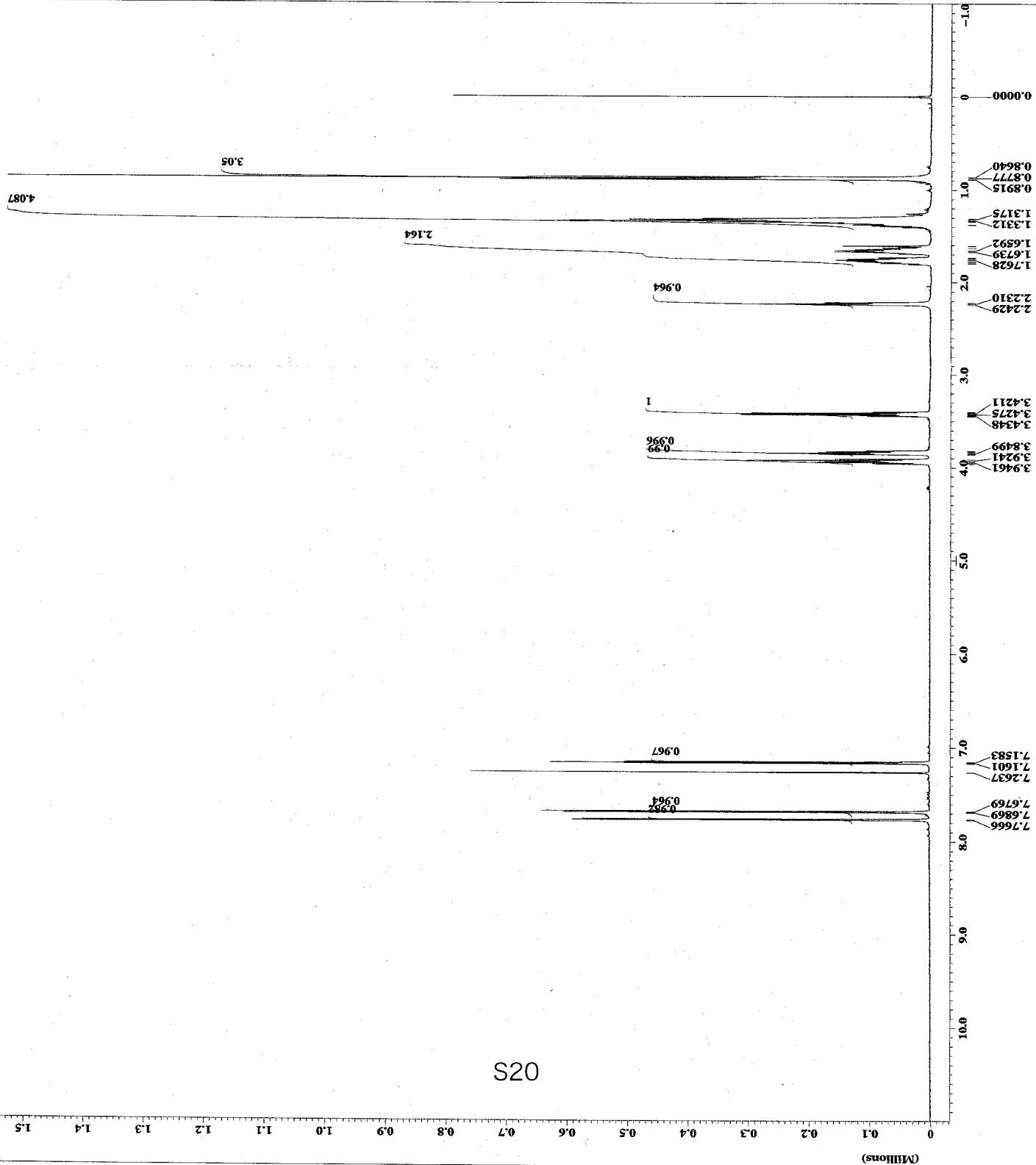


ACQUISITION PARAMETERS

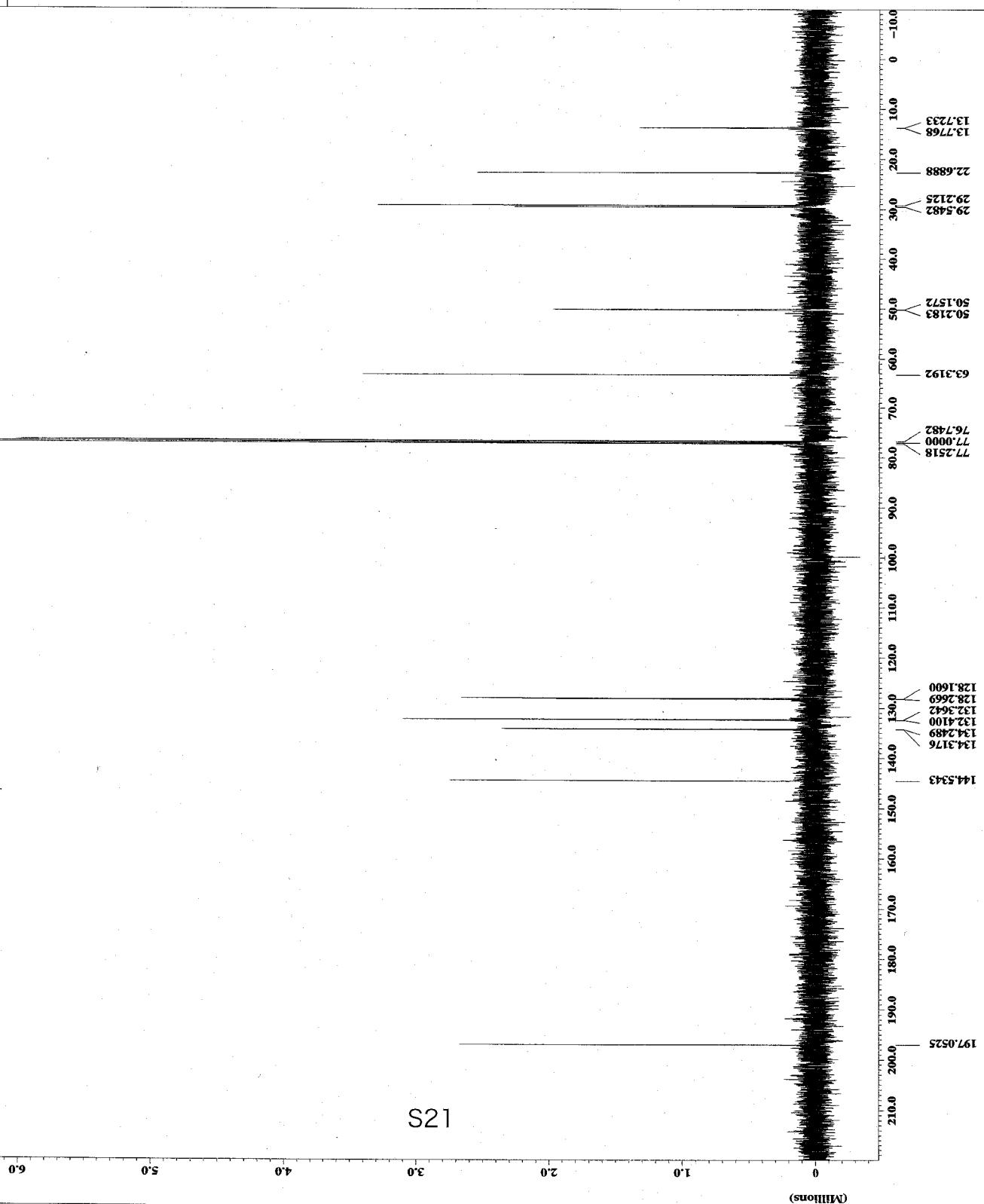
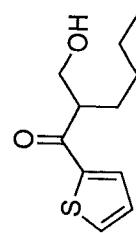
File Name = 1d.spectrum.43
 Author = 1H
 Sample ID = Single Pulse Experiment
 Context = 16-MAR-2007 11:55:53
 Creation Date = 18-MAR-2007 03:41:17
 Revision Date = ECP510
 Spec Site = DELTA_NMR
 Spec Type = 1D COMPLEX
 Data Format = 1D
 Dimensions = X
 Dim Title = 1H
 Dim Size = 16384
 Dim Units = [ppm]
 Scans = 8
 Block size = 1.
 No. of turns = 1.
 T1 refact = 5.0 [ppm]
 T2 refact = 7.5 [ppm]
 T3 refact = 7.50750751 [Hz]
 T4 refact = CHLOROTONE-D
 Solvent =
 Spin, get = 17 [Hz]
 Temp, get = 24.8 [dc]
 Nerve, gain = 15
 Field strength = 11.7473579 [T]
 Filter, mode = BUTTERWORTH
 Filter_width = 3.75119936 [kHz]



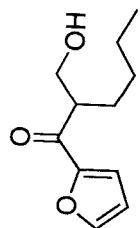
3g



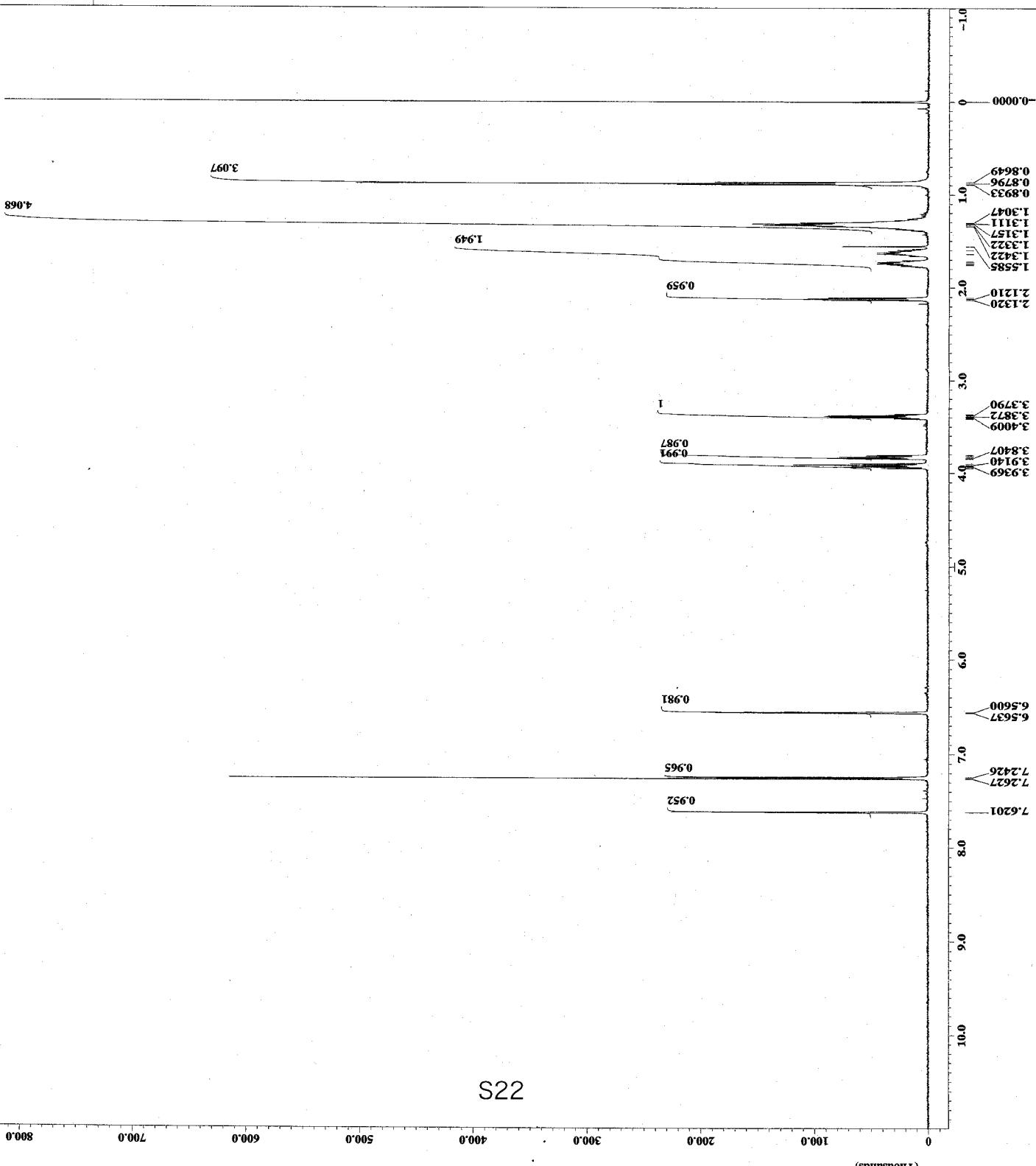
----- ACQUISITION PARAMETERS -----
 File Name = 1C_spectrum_82
 Author = 1C
 Sample ID = Single Pulse with Broad
 Contact = 25-MAR-2007 15:18:49
 Creation Date = 30-MAR-2007 05:06:01
 Revision Date = ECP500
 Spec Type = DEPTA_NMR
 Spec Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 1C
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 200
 Modulation = 100 [ppm]
 X_Offset = 125.77787547 [MHz]
 X_Freq = 31.44654088 [Hz]
 Solvent = CHLOROFORM-D
 Spin_get = 16 [Hz]
 Temp_get = 25.0 [degC]
 Recv_Gain = 15
 Field_Strength = 11.7473579 [T]
 Filter_Mode = BUTTERWORTH
 Filter_Width = 15.72056221 [Hz]



--- ACQUISITION PARAMETERS ---
File Name = 1d_spectrnm.98

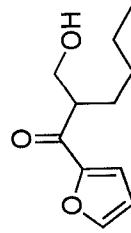


3

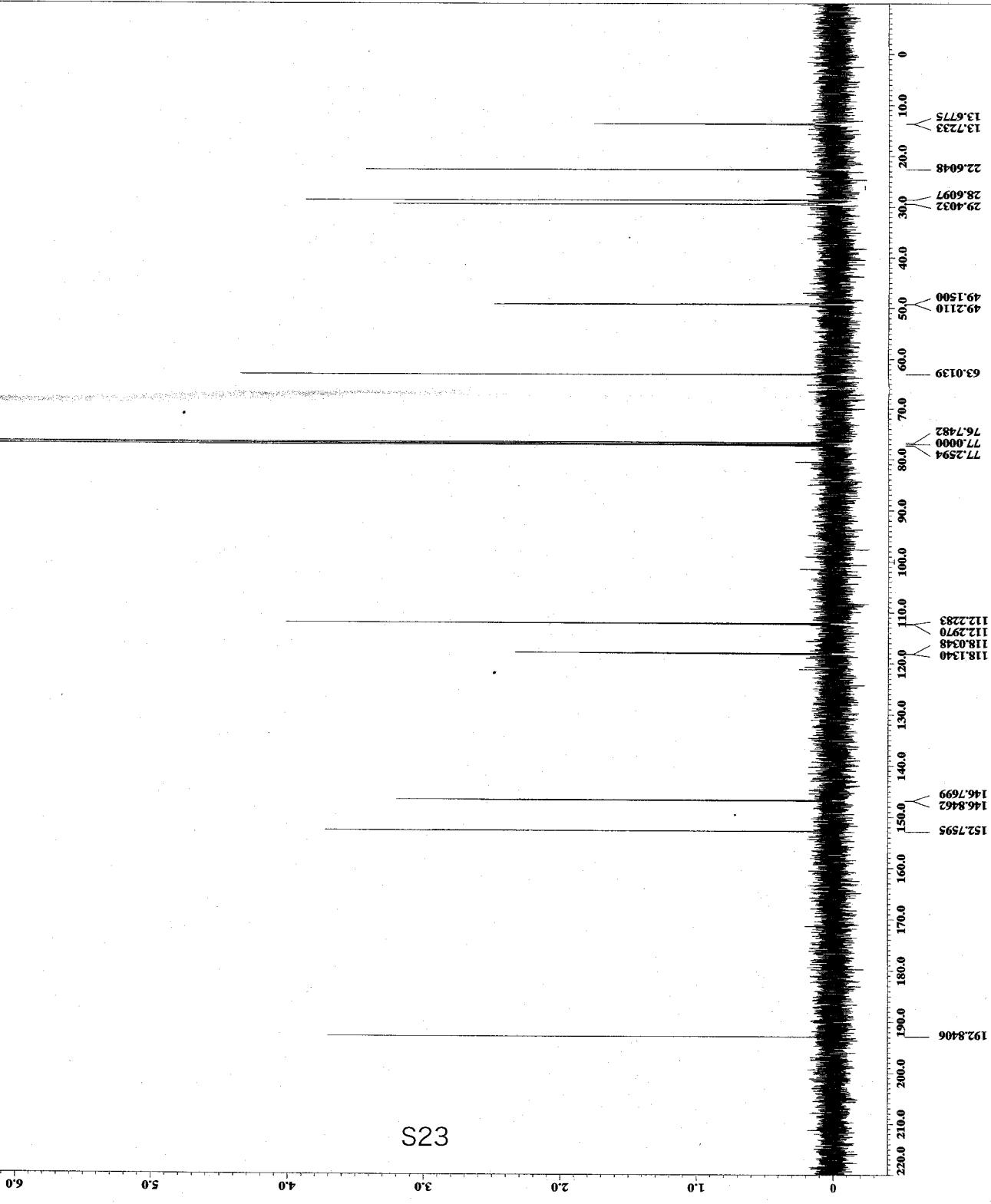


ACQUISITION PARAMETERS

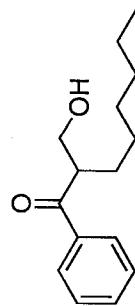
File Name : 14_13C_spectra.m 77
 Author :
 Sample ID : 13C
 Content : Single Pulse, with Broad
 Creation Date : 26-MAR-2007 19:42:31
 Revision Date : 26-MAR-2007 09:27:23
 Spec Site : ECP500
 Spec Type : DEPTA_NMR
 Data Format : 1D COMPLEX
 Dimensions : 1
 D1m 512.4 : 13C
 D1m 10.0 : 13C
 Scans : 200
 Mod. return : 1
 X_Offset : 100 [ppm]
 X_frog : 125.77787547 [MHz]
 X_sweep : 31.44654084 [Hz]
 Solvent : CHLOROPHEN-D₆
 Spin_get : 15 [Hz]
 Temp_get : 25.3 [deg]
 Recv_grain : 15
 Field_stretch : 11.73579 [T]
 Filter_mode : Butterworth
 Filter_width : 15.74066221 [Hz]



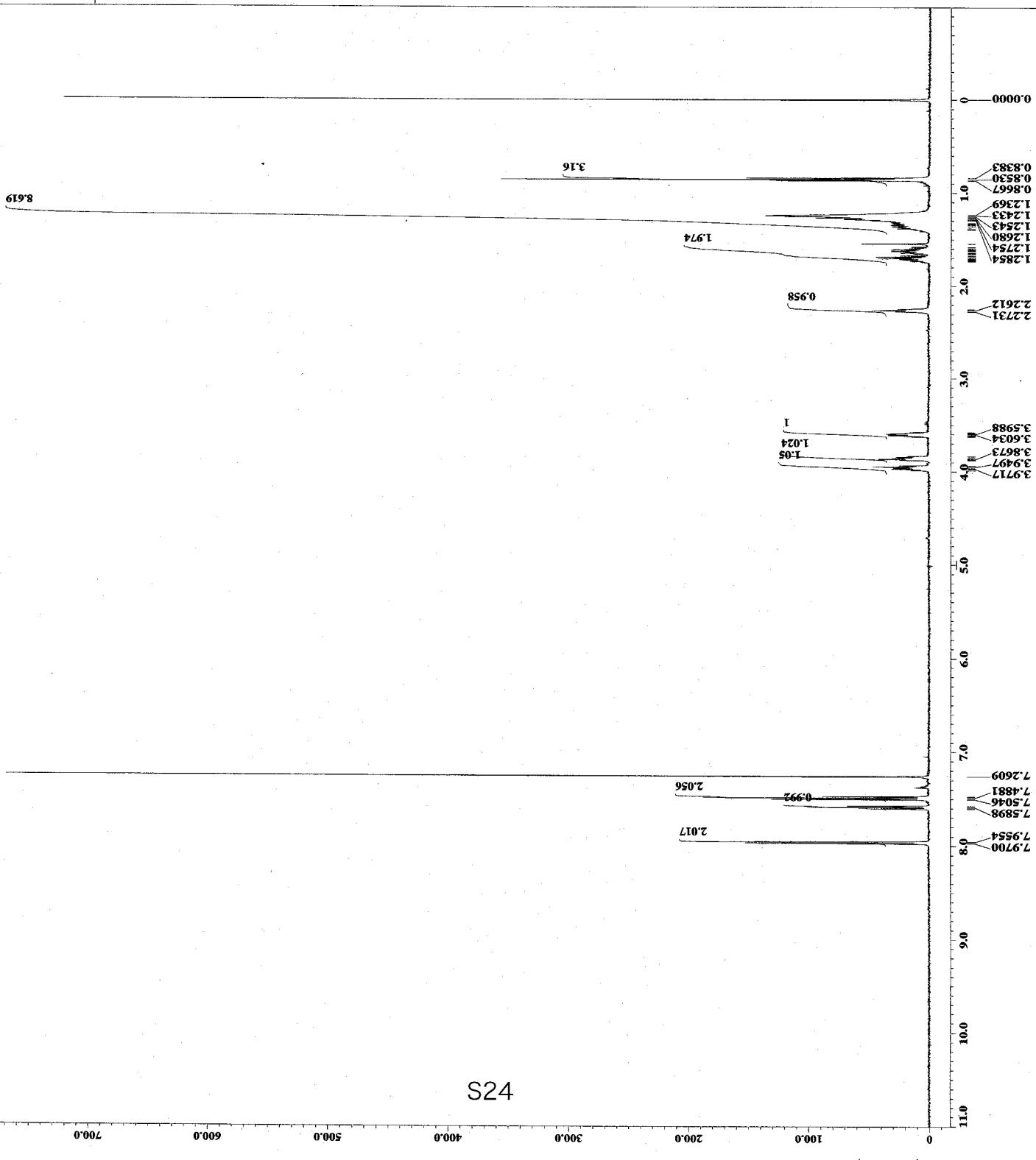
3h



ACQUISITION PARAMETERS
File Name = 1d_spectrum.104
Author =

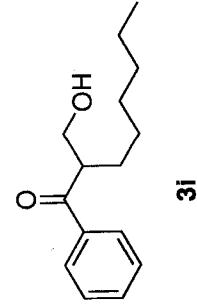
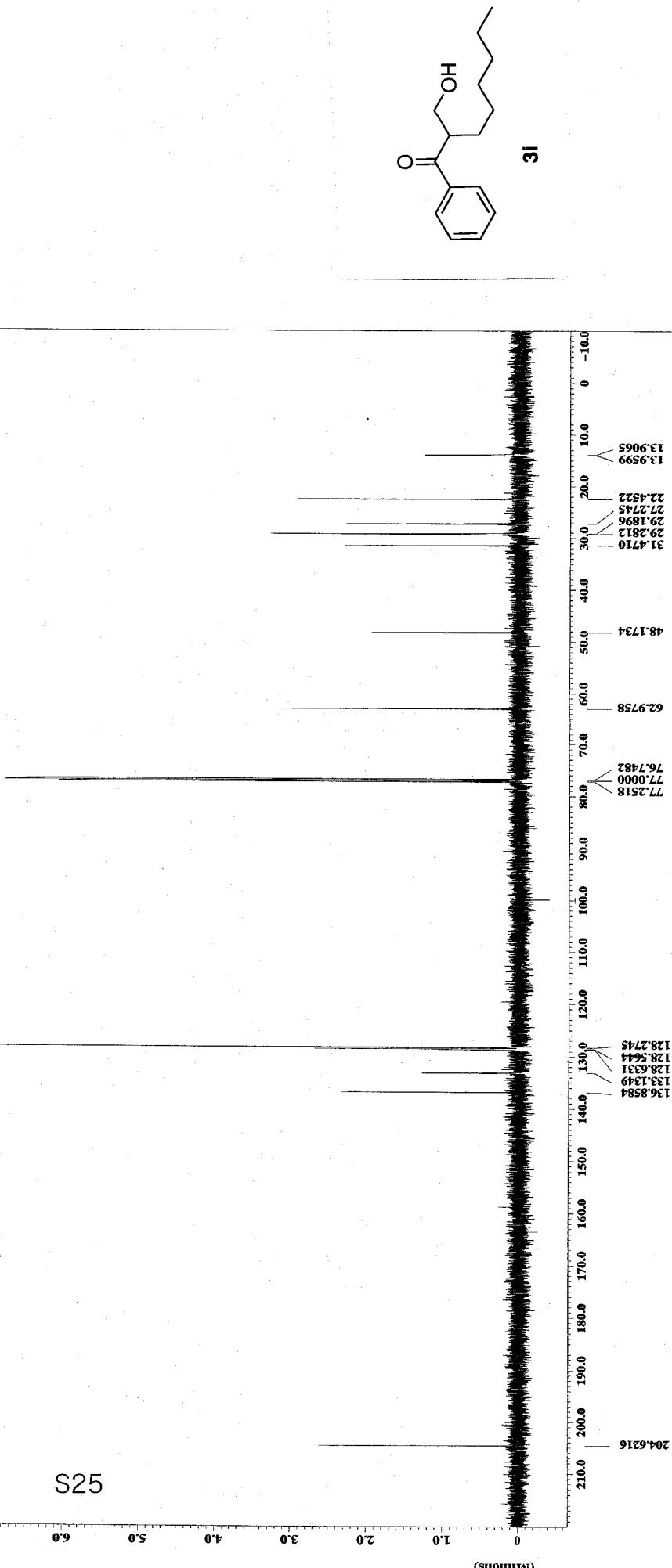


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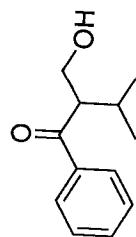
ACQUISITION PARAMETERS
 File Name = 1d_13c_spectrum_80
 Instrument = 13C
 Sample ID = Single Pulse with Broad
 Content = 28-MAR-2007 14:53:27
 Creation Date = 30-MAR-2007 04:40:26
 Revision Date = EXP500
 Spec Site = DRIFT_NMR
 Spec Type = 1D COMPLEX
 Data Format = X
 Dimensions = 13C
 Dim Title = 13C
 Dim Size = 32768
 Scan Cycles = 200
 Scan Return = 1
 Z-domain = 13C
 Z-offset = 100 [ppm]
 Z-freq = 135.77787547 [MHz]
 Z-sweep = 31.44654088 [Hz]
 Solvent = CHLOROFORM-D
 SpinGet
 Temp.Get
 Recv.Gain
 Field Strength = 11.7473579 [mT]
 Filter.Mode = SUPERBORN
 Filter.Width = 15.72066221 [Hz]



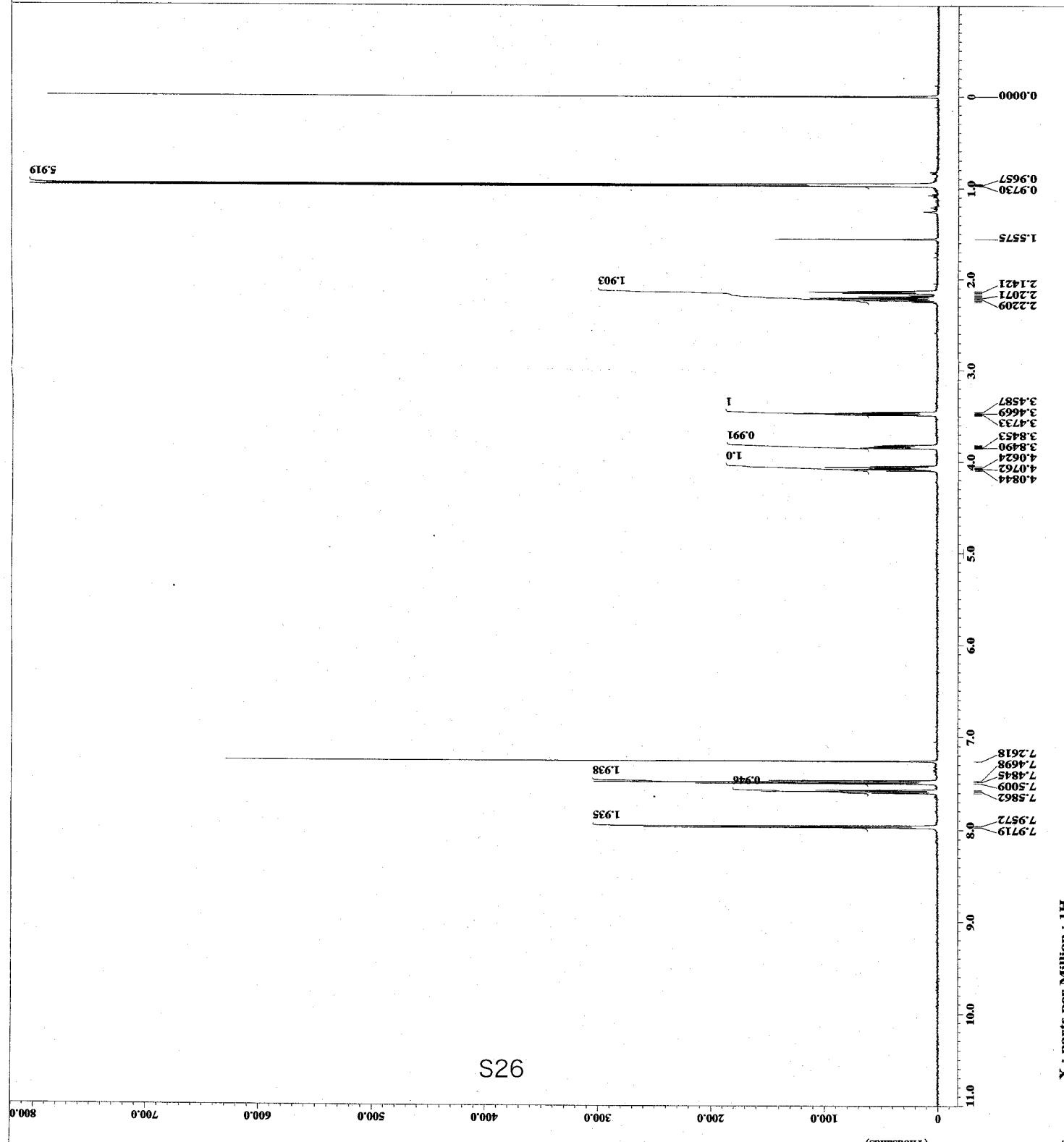
JEOL

ACQUISITION PARAMETERS

File Name	id_spectraun_55
Author	IH
Sample ID	Single Pulse Experiment
Content	16-MAX-2007 14:47:40
Creation Date	16-MAR-2007 04:23:38
Revision Date	16-MAR-2007 04:23:38
Spec Site	KCP200
Spec Type	CPMG
Data Format	ID COMPLEX
Dimensions	1H
Dim Title	
Dim Size	16384
Dim Units	[ppm]
Scans	8
Mod. return	1
X domain	1H
X offset	51ppm
X freq	301.1241652 [MHz]
Acq. time	20.000000 [sec]
Spinclock	1000000000 [Hz]
Spinbit	18 [Hz]
Temp. set	24.1 [°C]
Recrv. gain	15
Filter width	11.7473759 [Hz]
Filter order	3
Filter type	BUTTERWORTH
Filter width	3.75119336 [Hz]

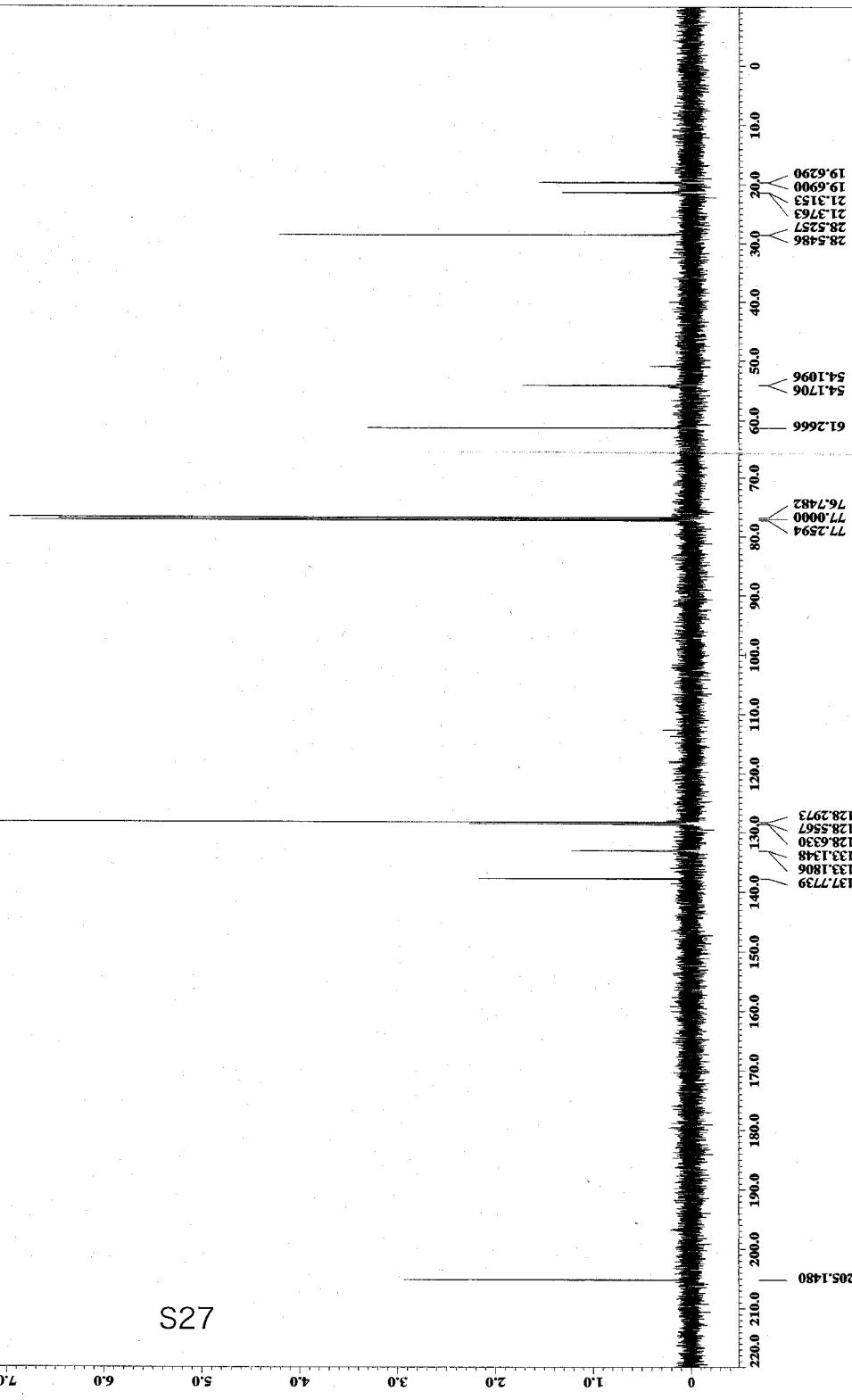
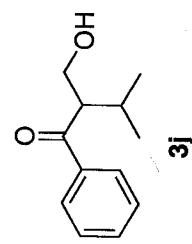


3



---- ACQUISITION PARAMETERS ----

File Name = id_13c_spectrum.88
 Author =
 Sample ID = 13C
 Content = Single Pulse with Broad
 Creation Date = 28-MAR-2007 16:12:41
 Revision Date = 30-MAR-2007 05:59:52
 Spec Site = ECSP500
 Spec Type = CP/MAS NMR
 Data Format = ID COREL LINK
 Dimensions = 13C
 Dm Title = 13C
 Dm Size = 32768
 Dm Units = [ppm]
 Scans = 200
 Mod. return = 1
 X-domain = 13C
 X-offset = 100 [ppm]
 X-freq = 125.7787557 [MHz]
 X_sweep = 31.4554089 [MHz]
 Solvent = CHLOROFORM-D
 Spin.get = 55 [Hz]
 2D_Spin = 15. [Hz]
 Recycle_min = 15. [sec]
 Preset_time = 11.7473579 [m]
 Field_strenght = 8.0 T
 Filter mode = BURSTBORN
 Filter_width = 15.720665221 [MHz]

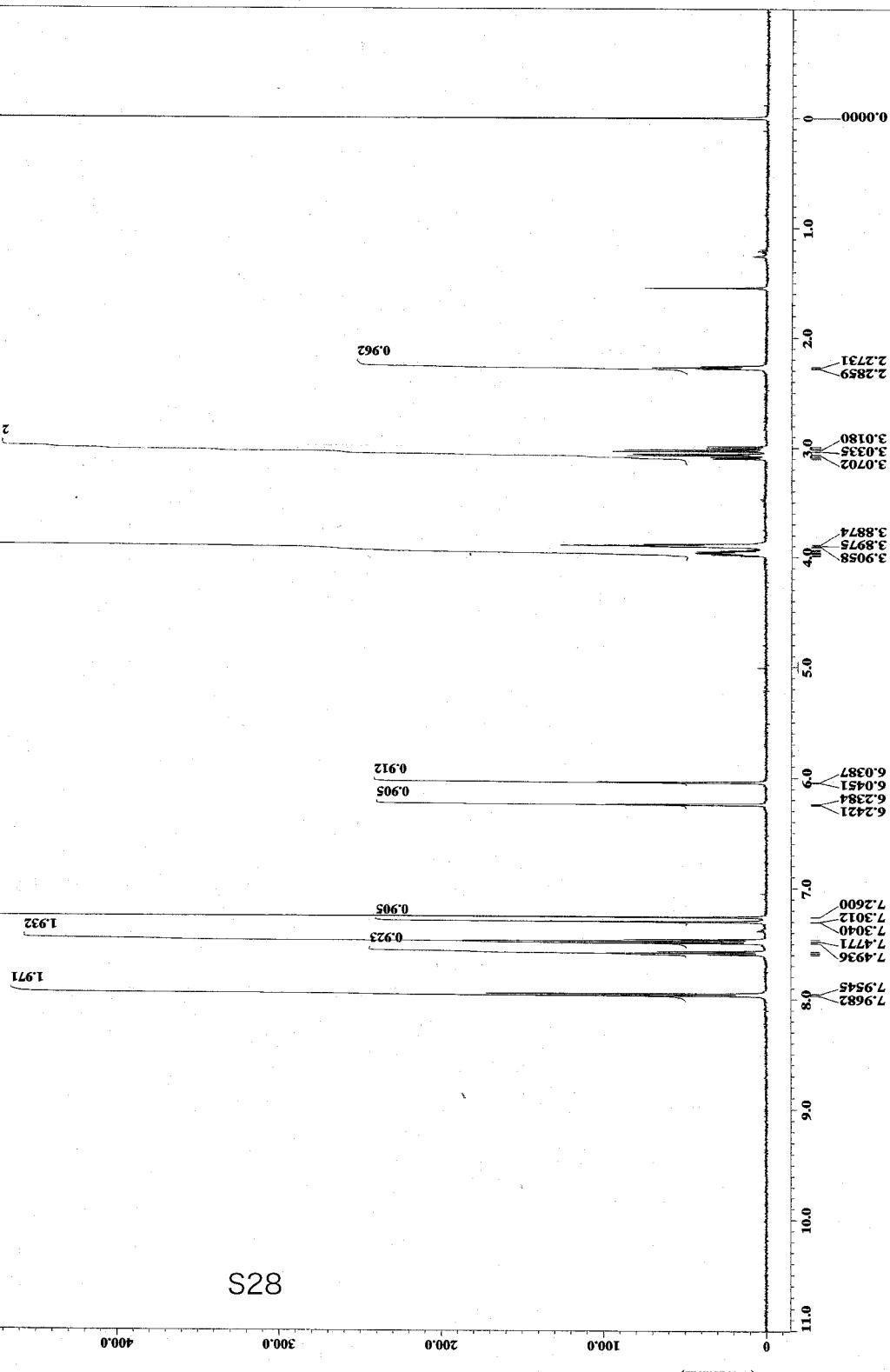
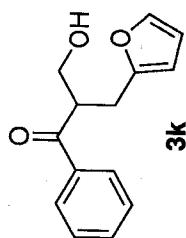


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----- ACQUISITION PARAMETERS -----
File Name = 1D_Spectrum.107
Author = 1H
Sample ID = Single Pulse Experiment
Content = 17-MAR-2007 11:03:15
Revision Date = 19-MAR-2007 00:19:53
Spec Site = ECP500

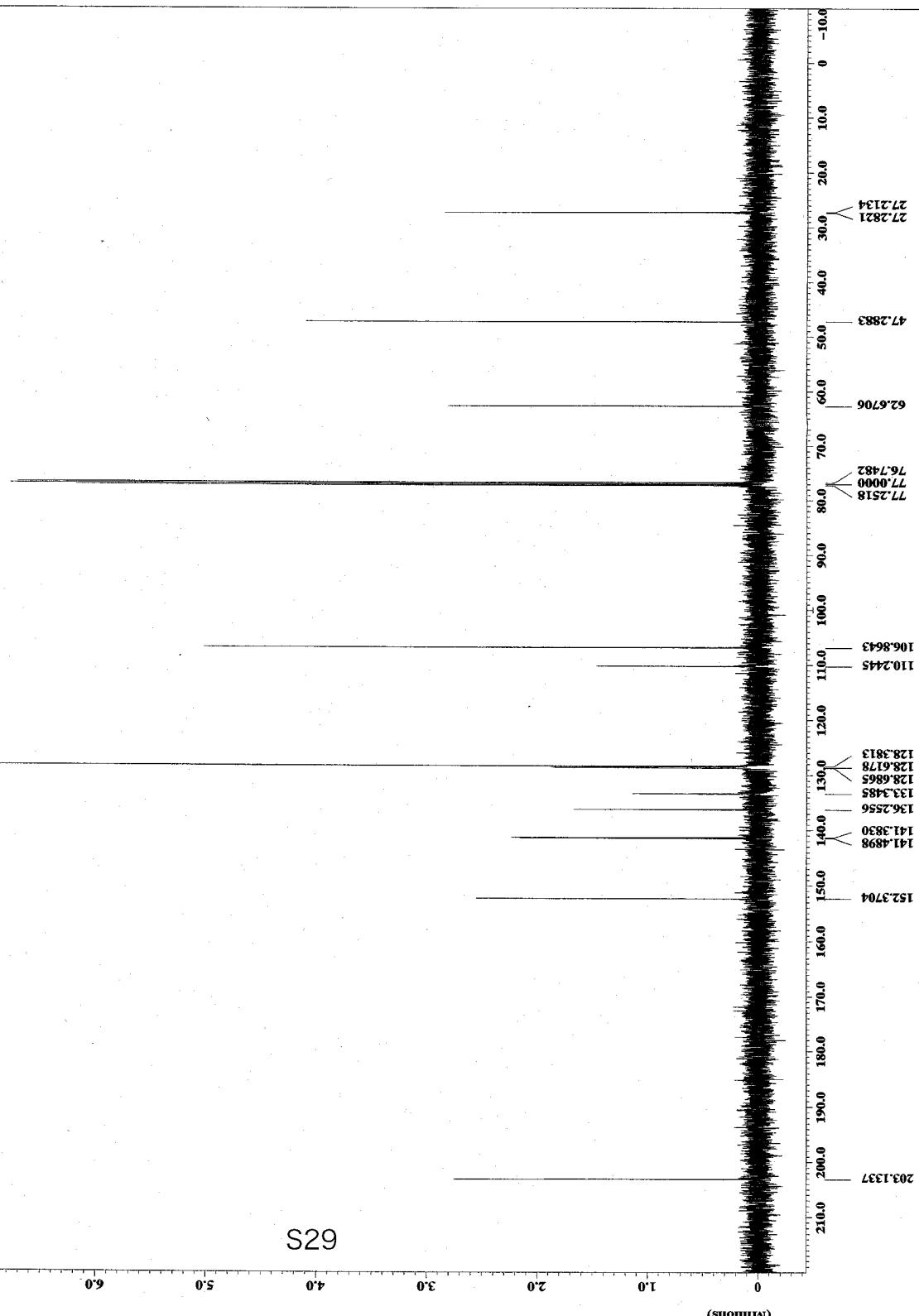
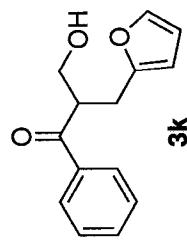
----- DELTA_NMR -----
Sample Format = COMPLEX
Dimensions = 1H
Title = 1H
Bin Size = 1.0384
Data Units = ppm
Scans = 8
Integration = 1H
Siginum = 1
Offset = 50.11241602 [MHz]
Lswpp = 7.50750751 [kHz]
Chloroform-D = 18 [Hz]
Spin get = 24 [rads]
Recygr. gain = 15
Filter strength = 11.7473579 [T]
Filter width = 3.75119336 [kHz]

```



ACQUISITION PARAMETERS

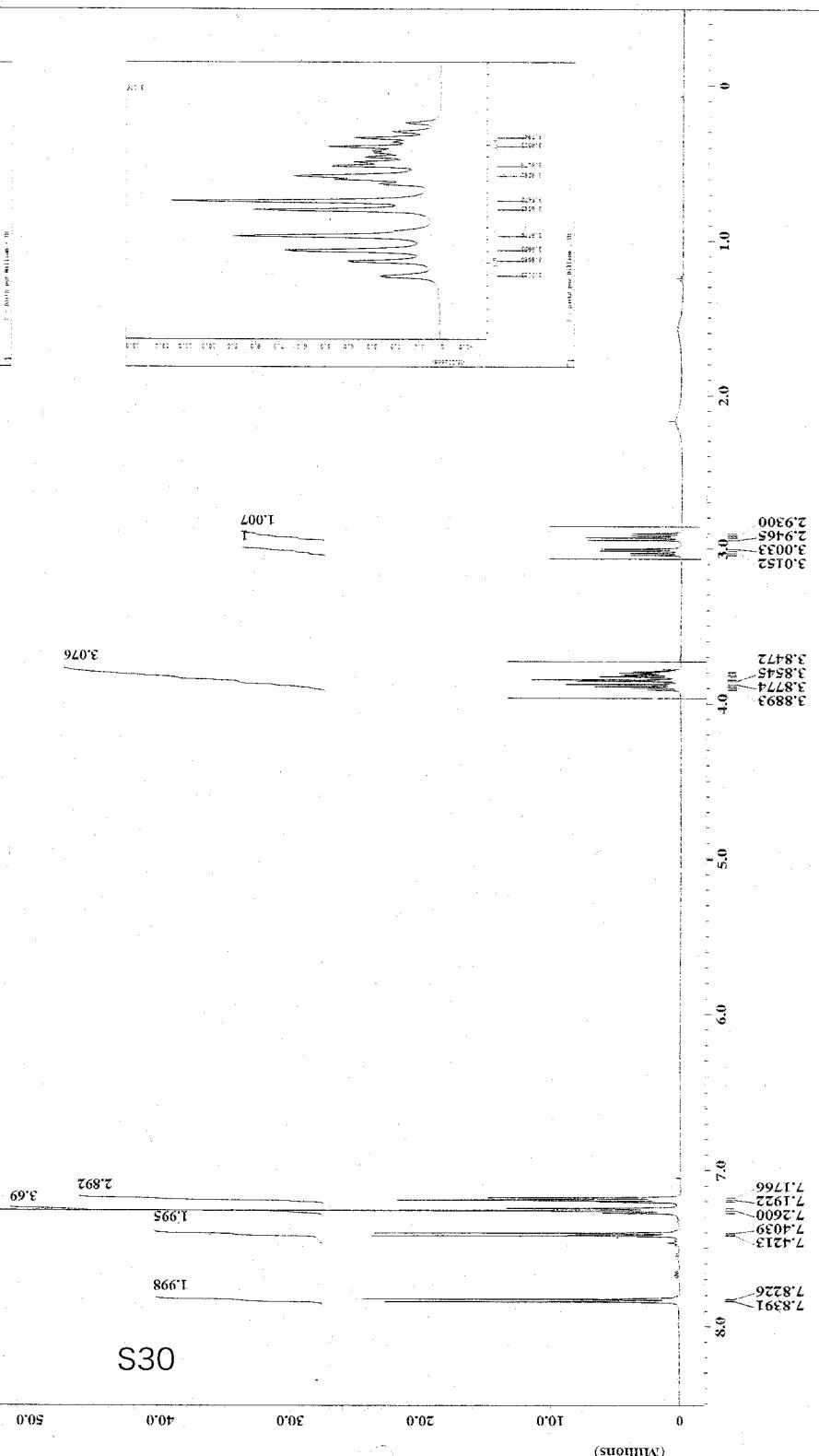
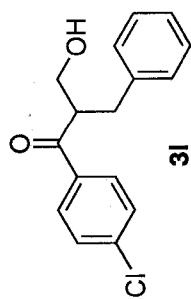
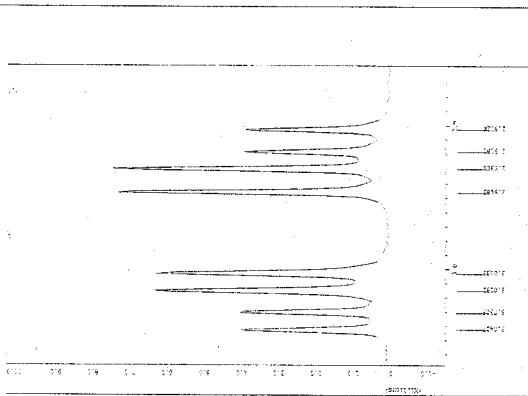
File Name = 1d_13c_spectrum_78
 Author =
 Sample ID = 13C
 Content = Single Pulse with Broad
 Creation Date = 26-MAR-2007 19:57:32
 Revision Date = 28-MAR-2007 09:41:43
 Spec Site = ECP500
 Spec Type = DEPTA, NMR
 Data Format = 1D COMPLEX
 Dimensions = 1,3C
 Dim Title =
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 200
 Mod. return = 1
 X-domain = 13C
 X_Offset = 100 [ppm]
 X_Freq = 125.77787547 [MHz]
 X_Sweep = 31.44654088 [kHz]
 Solvent = CHLOROFORM-D
 Spin_Get = 1 [Hz]
 Temp_Gain = 24.7 [dc]
 Acqv_Gain = 15
 Prog_Smooth = 1.7473579 [m]
 Filter_Bandwidth = 8000 [Hz]
 Filter_Match = 125.72265622 [Hz]



JEOL

ACCOUNTING PARAMETERS ----

File Name	1d_spectrum_7.75s
Author	= "S#310505"
Sample ID	Content
Creation Date	= "31-JUN-2008 15:03:22"
Revision Date	= "2-AUG-2008 14:58:02"
Spec Site	= ECP500
Spec Type	= DEPR, NMR
Dimensions	= 1D, COMPLEX
Dim. #1	= X
Dim. Size	= 1H
Dim. Units	= 16.84
Scans	= 8
Mod. Return	= 1
X-domain	= 1H
X-offset	= 5 ppm
X-Freq	= 16.241000 [MHz]
Sweep	= 500.000000 [Hz]
Scan	= CR0.0507515 [Hz]
Spin	= 1.000000 [ppm]
Temp. set.	= -16.000000 [K]
Refr. gain	= 30
Field strength	= 11.74735791 [T]
Filter mode	= BUTTERWORTH
Filter width	= 3.75119936 [kHz]

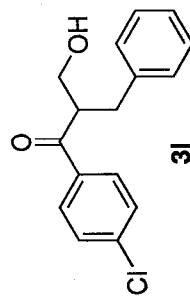


ACQUISITION PARAMETERS

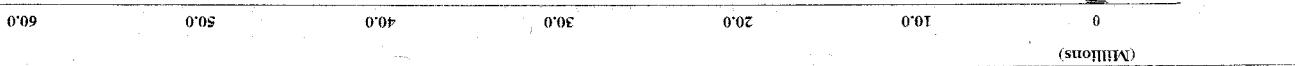
```

File Name = 1d_13c_spectrun_76
Number = 0
Sample ID = av432chb2
Content = Single Pulse with ESRoad
Creation Date = 29-JUL-2008 14:19:26
Revision Date = 31-JUL-2008 14:07:51
Spec Size = EXP500

Spec Type = DELTA_NMR
Data Format = 1D COMPLEX
Dimensions = X
Data Title = 13C
Data Size = 32768
SCN in Silits = 71
Nod return = 1
Xdomain = 13C
X_offset = 100 [ppm]
X_freq = 135.77787547 [MHz]
X_sweep = 31.44654088 [Hz]
Solvent = CHLOROFORM-D
Spin.get = 17 [Hz]
Temp_get = 27.3 [dc]
Reevr.grain = 30
Field.strength = 11.747579 [mT]
Filter.mode = BURGEROTH
Filter.width = 15.7206221 [Hz]
```



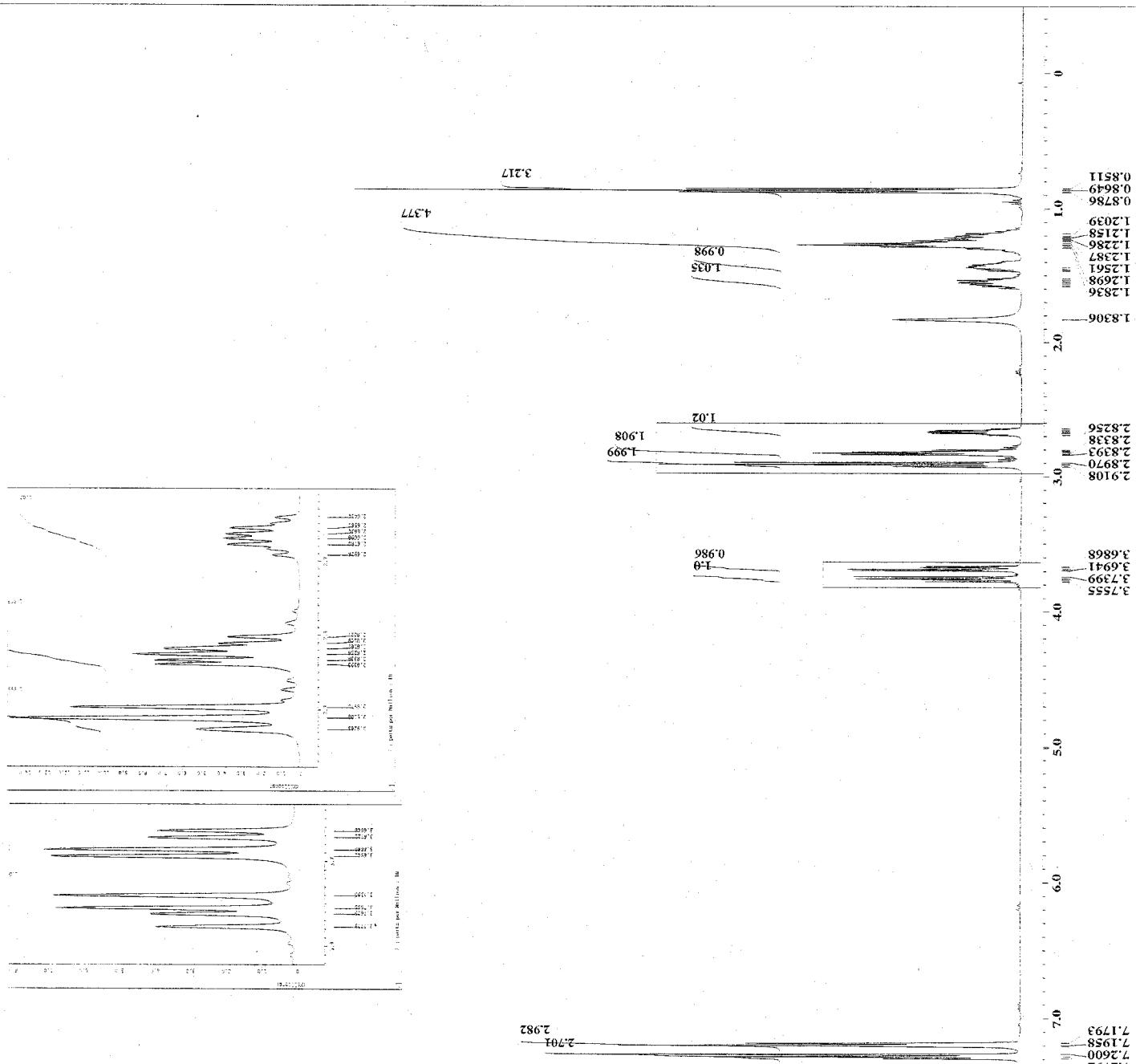
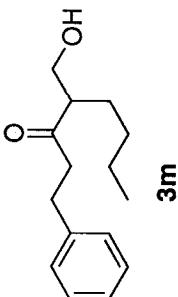
13S



X : parts per Million : 13C.

(MHz)

JEO



S32

0 0.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0 29.0 30.0 31.0 32.0 33.0 34.0 35.0 36.0 37.0 38.0 39.0 40.0

FILE C:\WINNMR98\COMMON\DEFAULT.ALS
COMMENT au433c2h4
DATE Mon Aug 04 19:08:04 2008
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 kHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27210.88 Hz
SCANS 21
ACQTM 1.2042 sec
PD 1.7940 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 25

